EORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL

[ ] REVISION NO.

roject No. E-20-685 — DATE: 7/29/81

roject Director: Dr. W. H. Cross/~~Dr. E.S.K. Chian~~ DR. CHIAN ~~Dr. SAUNDERS~~ — School/Lab: ~~xxx~~ Civil Engineering

ponsor: Department of Energy, Grand Forks Energy Technology Center

ype Agreement: Contract No. DE-~~AC18~~AC21-81FC10297 ~~8-30-85~~ ~~2-30-85~~ 8-30-85

ward Period: From 7/1/81 To ~~12/31/82~~ 8-30-85 (Performance) 12/31/82 (Reports)

ponsor Amount: $199,980 (incrementally funded at $73,000 thru 12/31/81) — Contracted through: N/A

ost Sharing: N/A — GTRI/~~xxx~~

itle: Anaerobic Treatment of Gasifier Effluents

ADMINISTRATIVE DATA — OCA CONTACT: Faith G. Costello

1) Sponsor Technical Contact: Mr. Leland Paulson, DOE, Grand Forks Energy Technology Center, Box 8213, University Station, Grand Forks, ND 58201 (701) 795-8165

2) Sponsor Admin./Contractual ~~Contact~~: ~~Mr. Joseph Bogus,~~ PAUL R. BERNS Contract Specialist, DOE PROJ. OFFICE Grand Forks ~~Energy Technology Center~~, Box ~~8213,~~ 7206 University Station, Grand Forks, ND 58201 58202

Reports: See Deliverable Schedule — Security Classification: N/A

Defense Priority Rating: N/A

RESTRICTIONS

See Attached Government Supplemental Information Sheet for Additional Requirements

Travel: Foreign travel must have prior approval - Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with Government; except that items costing less than $1,000 shall vest with GIT upon acquisition, provided prior approval obtained from sponsor.

COMMENTS:

AUG 1981 RECEIVED Research Reports Office

COPIES TO:

Administrative Coordinator
Research Property Management
Accounting Office
Procurement/EES Supply Services
Research Security Services
~~Reports~~ Coordinator (OCA)
Legal Services (OCA)
Library, Technical Reports
EES Research Public Relations
Project File (OCA)
Other:

:ORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 4-15-87

ject No. E-20-685 School/Lab ~~XXXX~~ CE

ludes Subproject No.(s) N/A

ject Director(s) Drs. Cross and Chian GTRC / ~~GIT~~

onsor Department of Energy, Grand Forks Energy Technology Center

le Anaerobic Treatment of Gasifier Effluents

ective Completion Date: 8/30/86 (Performance) 8/30/86 (Reports)

ant/Contract Closeout Actions Remaining:

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [X] Closing Documents
- [X] Final Report of Inventions - Questionnaire sent to P.I.
- [X] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

ntinues Project No. Continued by Project No.

PIES TO:

ject Director
search Administrative Network
search Property Management
counting
ocurement/GTRI Supply Services
search Security Services
[redacted]
[redacted]

Library
GTRC
[redacted]
Project File
Other Duane H.
Angela DuBose
Russ Embry

IBM OCA 69-285

Georgia Institute of Technology
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
ATLANTA, GEORGIA 30332

SCHOOL OF
CIVIL ENGINEERING

TELEX: 542507 GTRC OCA ATL

TELEPHONE
(404) 894-2265

May 14, 1986

MEMORANDUM

TO: Office of Contract Administration

FROM: Dr. Wendall Cross
Civil Engineering

RE: Project Reports on E20-685

Attached are copies of the, July 1985 through November 1985, monthly project status reports which have been sent regularly to U.S. DOE - Grand Forks and a copy of the extension of the contract to August 31, 1986.

All experimental work on the project was completed in November 1985. The draft final report is being prepared and should be available in early June 1986.

If you have any questions or need additional information, please contact me accordingly.

/hb
Attachments
cc: J. E. Fitzgerald, w/o attachments
W. M. Sangster, w/o attachments

AN EQUAL EDUCATION AND EMPLOYMENT OPPORTUNITY INSTITUTION

GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

TITLE Anaerobic Treatment of SFBG Wastewater

PERIOD ENDING July 31, 1985

GFPO MANAGER Leland E. Paulson

COMPILED BY Wendall Cross, Georgia Tech

PTPA NO. 4-641

B&R NO. AA8540000

PIP NO. 18-83FC10297

ACCOUNT CODES CK

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater

- PERIOD ENDING July 31, 1985

FY OBJECTIVES

The project involves treating ammonia stripped slagging fixed bed gasification wastewater by an upward flow anaerobic carbon filter followed by nitrification and denitrification process. Project objectives include:

- Determination of maximum treatable concentration of organics in the wastewater.
- Investigate the feasibility of removing nitrogen compounds after carbon filter process.
- Investigate feasibility of biodegradation of water soluble hydantoin.
- Determination of organic components that inhibit anaerobic treatment.

Specifically for FY 85:

1. Complete identification of inhibitory compounds in wastewater.
2. Complete method development for regeneration of spent carbon.
3. Complete biodegradation study of hydantoins.
4. Complete final report.

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

● TITLE Anaerobic Treatment of SFBG Wastewater

● PERIOD ENDING July 31, 1985

FY ACCOMPLISHMENTS

Batch inhibition studies have been completed for seven major constituents found in slagging fixed bed gasifier effluents with no indication of inhibition at the concentrations investigated. (11/84)

Batch serum bottle studies also indicate that hydantoins are anaerobically degraded at long hydraulic retention times. (12/84)

Isotherm data for the adsorption of three different hydantoins on granular activated carbon have been obtained and carbon capacities are of the same order of magnitude as that of phenols on the same order of magnitude as that of phenols on the same carbon. (1/85)

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater
- PERIOD ENDING July 31, 1985

CURRENT AND POTENTIAL PROBLEMS

None

TRIPS AND VISITORS

None

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

● TITLE Anaerobic Treatment of SFBG Wastewater

● PERIOD ENDING July 31, 1985 CONTRACTOR Georgia Tech

TECHNICAL DISCUSSION

(This section includes this month's objectives, this month's accomplishments, and next month's objectives)

This Month's Objectives

1. Complete a 3rd adsorption-regeneration cycle with methanol as the regenerant.
2. Perform an adsorption-regeneration cycle using methyl-ethyl-ketone as the regenerant.
3. Monitor the anaerobic system for pseudo-steady state gas production and TOC removal. Each time pseudo-steady state has been achieved the feed composition will be changed by decreasing the glucose TOC by 40% and increasing the pretreated wastewater TOC by 20%.

This Month's Accomplishments

1. The third adsorption-regeneration cycle has been completed. Data from this cycle show that ~70% of the adsorbed hydantoins were removed during the regeneration cycle. The volume of methanol required for regeneration is only 14% of the volume of raw wastewater which was treated.
2. The adsorption cycle for the methyl-ethyl-ketone has been completed.
3. Feed to the anaerobic system is still 500 mg/L glucose TOC and 500 mg/L pretreated wastewater TOC. Low gas production, 0.65 L/day, continues. Removal percentages are 51% TOC and 78% hydantoins.

Next Month's Objectives

1. Complete the 1st methyl-ethyl-ketone regeneration and based upon the data obtained either perform an addition cycle with MEK or select another organic solvent (either 2-propanol or ethanol) for the next cycle.
2. Continue to monitor the anaerobic system for increased biological activity. If gas production does not increase, one last reseeding attempt will be made. If gas production increases, feed composition will be altered to high strength pretreated wastewater.

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater
- PERIOD ENDING August 31, 1985
- METC MANAGER Leland E. Paulson
- COMPILED BY Wendall Cross, Georgia Tech
- PTPA NO. 4-641
- B&R NO. AA8540000
- PIP NO. 18-83FC10297
- ACCOUNT CODES CK

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

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• PERIOD ENDING August 31, 1985

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- o Investigate feasibility of biodegradation of water soluble hydantoin.
- o Determination of organic components that inhibit anaerobic treatment.

Specifically for FY 85:

1. Complete identification of inhibitory compounds in wastewater.
2. Complete method development for regeneration of spent carbon.
3. Complete biodegradation study of hydantoins.
4. Complete final report.

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater

- PERIOD ENDING August 31, 1985

FY ACCOMPLISHMENTS

Batch inhibition studies have been completed for seven major constituents found in slagging fixed bed gasifier effluents with no indication of inhibition at the concentrations investigated. (11/84)

Batch serum bottle studies also indicate that hydantoins are anaerobically degraded at long hydraulic retention times. (12/84)

Isotherm data for the adsorption of three different hydantoins on granular activated carbon have been obtained and carbon capacities are of the same order of magnitude as that of phenols on the same order of magnitude as that of phenols on the same carbon. (1/85)

MORGANTOWN ENERGY TECHNOLOGY CENTER

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

• TITLE Anaerobic Treatment of SFBG Wastewater

• PERIOD ENDING August 31, 1985

TRIPS AND VISITORS

None

MORGANTOWN ENERGY TECHNOLOGY CENTER

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater
- PERIOD ENDING August 31, 1985

CURRENT AND POTENTIAL PROBLEMS

Hardware problems and the breaking of a gc analytical column have delayed the hydantoin analysis associated with the granular activated carbon regeneration using methylethyl ketone and 2-propanol.

A new analytical column has been packed and conditioned and the hardware problem has been repaired.

Analysis are now proceeding as usual.

Mechanical problems (power failure and subsequent pump failure) required shut down of the anaerobic actived carbon system.

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

• TITLE Anaerobic Treatment of SFBG Wastewater

• PERIOD ENDING August 31, 1985 CONTRACTOR: Georgia Tech

TECHNICAL DISCUSSION

(This section includes this month's objectives, this month's accomplishments, and next month's objectives.)

This Month's Objectives

1. Complete 1st methylethyl ketone regeneration and based upon data obtained either perform an additional cycle with MEK or select another organic solvet (either 2-proponol or ethanol) for the next cycle.

2. Continue to monitor the anaerobic system for increased biological activity. If gas production does not increase, one last reseeding attempt will be made. If gas production increases, feed composition will be altered to high strength pretreated wastewater.

This Month's Accomplishments

1. Methylethyl ketone regeneration was completed. However, analytical problem delayed obtaining data for the regeneration cycle.

2. Although relatively constant TOC and hydantoin removals through the anaerobic activated carbon filter continued, gas production remained low. Mechanical problems required shut down of the system.

Next Month's Objectives

1. Run an additional methylethyl ketone regeneration cycle.

2. Begin a 2-proponol regeneration cycle.

3. Began Draft Final Report.

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater
- PERIOD ENDING September 30, 1985
- METC MANAGER Leland E. Paulson
- COMPILED BY Wendall Cross, Georgia Tech
- PTPA NO. 4-641
- B&R NO. AA8540000
- PIP NO. 18-83FC10297
- ACCOUNT CODES CK

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- o Investigate feasibility of biodegradation of water soluble hydantoin.
- o Determination of organic components that inhibit anaerobic treatment.

0 Specifically for FY 85:

- o Complete identification of inhibitory compounds in wastewater.
- o Complete method development for regeneration of spent carbon.
- o Complete biodegradation study of hydantoins.
- o Complete final report.

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater

- PERIOD ENDING September 30, 1985

FY ACCOMPLISHMENTS

- o Batch inhibition studies have been completed for seven major constituents found in slagging fixed bed gasifier effluents with no indication of inhibition at the concentrations investigated. (11/84)

- o Batch serum bottle studies also indicate that hydantoins are anaerobically degraded at long hydraulic retention times. (12/84)

- o Isotherm data for the adsorption of three different hydantoins on granular activated carbon have been obtained and carbon capacities are of the same order of magnitude as that of phenols on the same order of magnitude as that of phenols on the same carbon. (1/85)

MORGANTOWN ENERGY TECHNOLOGY CENTER

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater
- PERIOD ENDING September 30, 1985

CURRENT AND POTENTIAL PROBLEMS

NONE

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

• TITLE Anaerobic Treatment of SFBG Wastewater

• PERIOD ENDING September 30, 1985

TRIPS AND VISITORS

NONE

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

• TITLE Anaerobic Treatment of SFBG Wastewater

• PERIOD ENDING September 30, 1985 CONTRACTOR: Georgia Tech

TECHNICAL DISCUSSION

(This section includes this month's objectives, this month's accomplishments, and next month's objectives.)

This Month's Objectives:

1. Run an additional methyethyl ketone regeneration cycle.
2. Begin a 2-propanol regeneration cycle.
3. Begin draft final report.

This Month's Accomplishments:

1. Methyethyl ketone regeneration cycles have been completed.
2. One 2-propanol regeneration cycle has been completed.
3. An outline of the draft final report has been done.

Next Month's Objectives:

1. Complete an additional 2-propanol regeneration cycle.
2. Continue with draft final report.

GRAND FORKS PROJECT OFFICE - LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

TITLE Anaerobic Treatment of SFBG Wastewater

PERIOD ENDING October 31, 1985

METC MANAGER Leland E. Paulson

COMPILED BY Wendall Cross, Georgia Tech

PTPA NO. 4-641

B&R NO. AA8540000

PIP NO. 18-83FC10297

ACCOUNT CODES CK

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

ITLE . Anaerobic Treatment of SFBG Wastewater

ERIOD ENDING October 31, 1985 CONTRACTOR: Georgia Tech

TECHNICAL DISCUSSION

s section includes this month's objectives, this month's accomplishments, and next month's objectives.)

This Month's Objectives:

1. Complete an additional 2-propanol regeneration cycle.
2. Continue with draft final report.

This Month's Accomplishments:

1. 2-propanol regeneration cycle is complete and GC analysis of samples is underway.

2. Draft final report has been outlined.

Next Month's Objectives:

1. Conclude all regeneration data acquisition.
2. Continue with draft final report.

'LE Anaerobic Treatment of SFBG Wastewater

RIOD ENDING October 31, 1985

TRIPS AND VISITORS

W. H. Cross gave a presentation on the adsorption of pure hydantoins on ınular activated carbon at a conference: Energy for the Americas in San Juan, ., October 13-19, 1985.

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

TLE Anaerobic Treatment of SFBG Wastewater

ERIOD ENDING October 31, 1985

CURRENT AND POTENTIAL PROBLEMS

The principal investigators involvement in attending a conference, making a presentation and attending a one week short course has resulted in a delay in preparation of the draft final report.

MONTHLY STATUS REPORT

- TITLE Anaerobic Treatment of SFBG Wastewater

- PERIOD ENDING October 31, 1985

FY ACCOMPLISHMENTS

- Batch inhibition studies have been completed for seven major constituents found in slagging fixed bed gasifier effluents with no indication of inhibition at the concentrations investigated. (11/84)

- Batch serum bottle studies also indicate that hydantoins are anaerobically degraded at long hydraulic retention times. (12/84)

- Isotherm data for the adsorption of three different hydantoins on granular activated carbon have been obtained and carbon capacities are of the same order of magnitude as that of phenols on the same order of magnitude as that of phenols on the same carbon. (1/85)

GRAND FORKS PROJECT OFFICE • LARAMIE PROJECT OFFICE

MONTHLY STATUS REPORT

TITLE Anaerobic Treatment of SFBG Wastewater

PERIOD ENDING October 31, 1985

FY OBJECTIVES

0 The project involves treating ammonia stripped slagging fixed bed gasification wastewater by an upward flow anaerobic carbon filter followed by nitrification and denitrification process. Project objectives include:

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0 Specifically for FY 85:

- o Complete identification of inhibitory compounds in wastewater.
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RAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
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RAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
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● **TITLE** Anaerobic Treatment of SFBG Wastewater

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MORGANTOWN ENERGY TECHNOLOGY CENTER AND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE MONTHLY STATUS REPORT

● **TITLE** Anaerobic Treatment of SFBG Wastewater

● **PERIOD ENDING** November 30, 1985

FY ACCOMPLISHMENTS

Five solvents have been evaluated for the regeneration of exhausted granular activated carbon used to remove hydantoins from solvent extracted-ammonia stripped slagging fixed bed gasifier wastewater (11/85).

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

● TITLE Anaerobic Treatment of SERG Wastewater

● PERIOD ENDING November 30, 1985 CONTRACTOR: Georgia Tech

TECHNICAL DISCUSSION

(This section includes this month's objectives, this month's accomplishments, and next month's objectives.)

This Month's Objectives:

1. Conclude all regeneration data aquisition.
2. Continue with draft final report.

This Month's Accomplishments:

1. All regeneration data has been obtained and plotted.
2. Draft final report has been started.

Next Month's Objectives:

1. Continue work on final report.

MORGANTOWN ENERGY TECHNOLOGY CENTER
GRAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- **TITLE** Anaerobic Treatment of SFBG Wastewater
- **PERIOD ENDING** November 30, 1985

CURRENT AND POTENTIAL PROBLEMS

Draft final report will not be completed until late January or February.

MORGANTOWN ENERGY TECHNOLOGY CENTER
RAND FORKS PROJECT OFFICE ● LARAMIE PROJECT OFFICE
MONTHLY STATUS REPORT

- **TITLE** Anaerobic Treatment of SFBG Wastewater
- **PERIOD ENDING** November 30, 1985

TRIPS AND VISITORS

None

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
IL ENGINEERING

TELEPHONE
(404) 894-2265

December 8, 1981

Dr. Leland E. Paulsen
Grand Forks Energy Technology Center
Box 8213 University Station
Grand Forks, N. D. 58202

Dear Lee:

This is to keep you abreast of the progress of the anaerobic treatment of gasifier effluents. Attached is a brief summary of gas production, TOC removals, influent pH and alkalinity, ORP measurements and volatile acid concentrations.

Acclimation is still proceeding and complete methanogenesis has not been attained. Conversion of the substrate to volatile acids seems to be proceeding quite well. Conversion of volatile acids to methane is still incomplete. However, analysis of other specific compounds in the final effluent has not been initiated at this time.

Changes in operating procedures which have been initiated include: a) deletion of glucose from the nutrient buffer solution, b) deletion of the vitamin extract from the nutrient buffer solution. In addition we are in the process of converting to a single reservoir, single feed pump arrangement for each system. We feel that this will stabilize the pH, alkalinity and TOC of the influent and allow better control of the treatment system. The head space in the feed reservoir will be nitrogen purged to minimize dissolved oxygen in the feed.

Design of the solvent extraction system has begun and materials are being evaluated for its construction.

You will be receiving the more detailed quarterly report in January and we are all looking forward to your visit the first part of the year. If you have any questions concerning the progress of the project or if you need more detailed data please call me accordingly.

Sincerely yours,

Wendall H. Cross
Research Scientist
Project Director

WHC/hb

attachment

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Average values (mg/l) for the period November 6 through November 27

	System 1			System 2		
Parameter	Influent	Raschig Ring Effluent	Carbon Column Effluent	Influent	Raschig Ring Effluent	Carbon Column Effluent
TOC	796	637	288	994	851	433
Phenol	120	107	0	145	147	0
Total Volatile Acids	40	170	650	42	272	542

STATUS REPORT- PROJECT E-20-685 COAL GASIFICATION ANAEROBIC FILTER STUDY

DEC. 3, 1981

ACCLIMATION

Systems I and II seem to be acclimating satisfactorily; gas production is increasing in all columns except 1R. For a period of 10 days, from Nov. 5 to Nov. 15, the column was exhibiting negative gas production. This seemed to indicate a leak in the gas collection system, consequently the system was inspected closely and all tube clamps were tightened. The production rate has increased, but has not returned to its pre-Nov.5 level. A negative production rate was also noted on Nov. 30- thus the entire gas collection system will be reassembled with new tubing by Dec. 10.

The average gas production rate for each column is:
1R-120 cc/day (formerly around 500 cc/day)
1A-370 cc/day
2R-1820cc/day
2A-490 cc/day

FEED SOLUTIONS

The diluent buffer is prepared every six days. The nutrient solution has not been added to the buffer since Oct. 31, the last tank of nutrient buffer was depleted on Nov. 5. Buffer preparation dates are indicated on the pH graph, along with raw waste addition dates and other significant events.

Note that 10 gals. of raw wastewater and 10 gals. of tap water were added to the feed tank on Nov. 27, andcaused an increase in both pH and Alkalinity.

Note also that the influent pH varies with diluent buffer preparations. Perhaps this variation can be eliminated by stabiliation with phosphoric acid to a more neutral pH.

MONITORING

Gas production is measured daily, results are shown in fig.1.
pH and Alkalinity are measured twice a week, results are shown in figures 2 and 3, respectively.
ORP cells have not arrived for the Carbon filter effluents yet, however ORP is measured in the roughing filters twice a week:
2R has been steadily averaging around -430 mV
1R has been averaging around -420 mV, but dropped to -340 as read Dec.1.

SYSTEM III

The columns and media for system III have been cleaned. The columns are assembled and mounted. The gas collection system is currently under assembly, and the feed and recycle systems will be assembled the weeks of Dec.10-21.

FIG.1

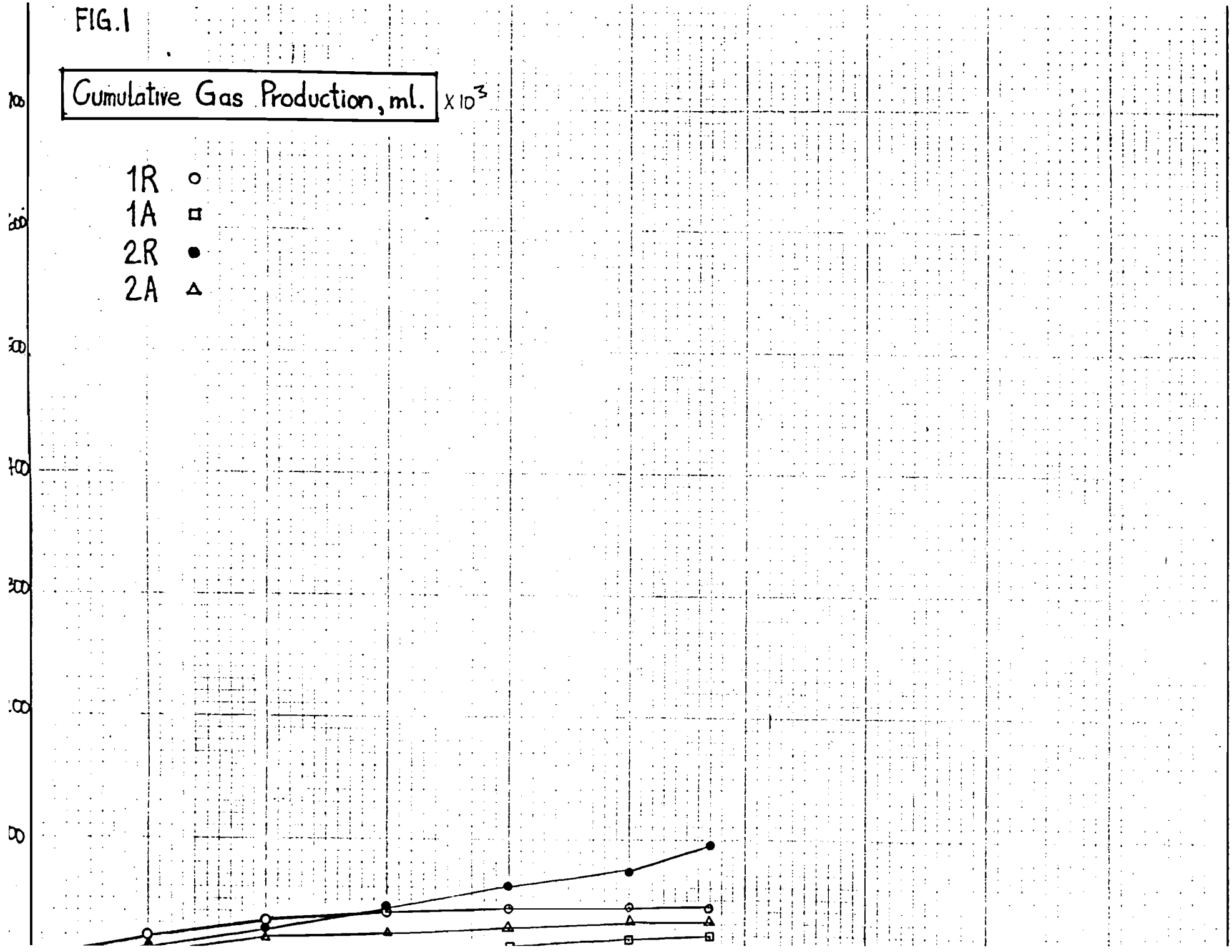


FIG. 2

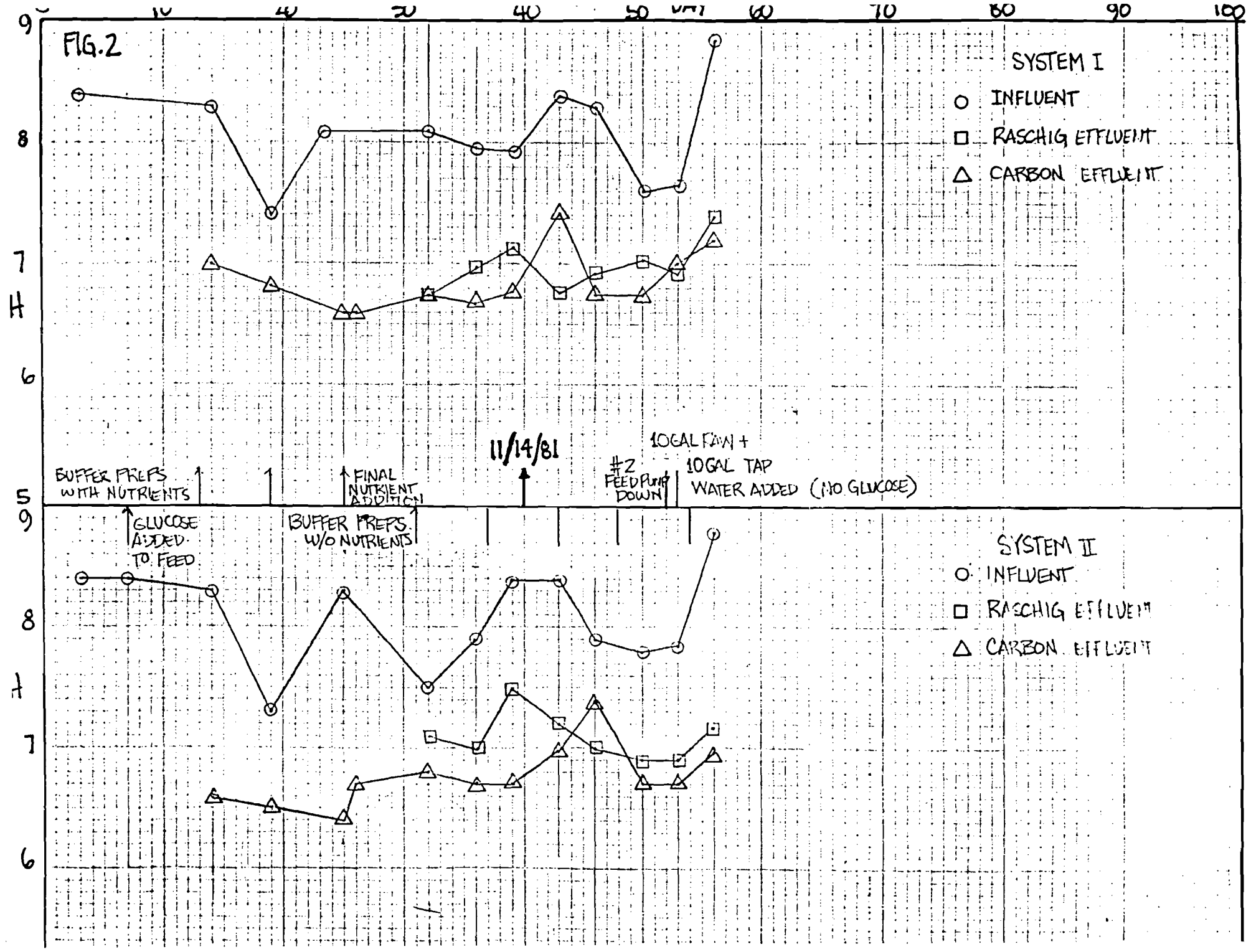
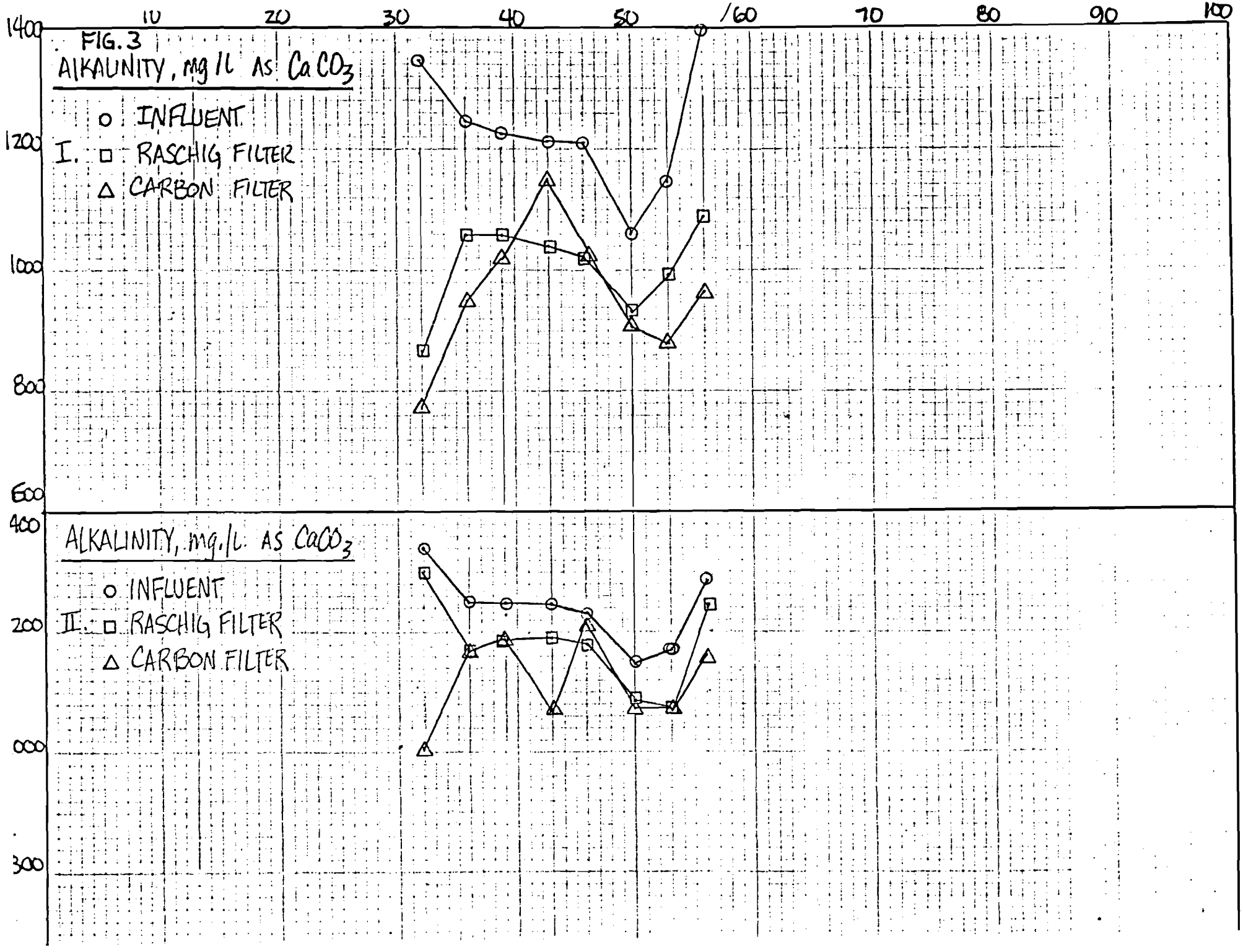

SYSTEM I
INFLUENT
RASCHIG EFFLUENT
CARBON EFFLUENT
BUFFER PREPS WITH NUTRIENTS
FINAL NUTRIENT ADDITION
11/14/81
#2 FEED PUMP DOWN
10 GAL FAN + 10 GAL TAP WATER ADDED (NO GLUCOSE)
GLUCOSE ADDED TO FEED
BUFFER PREPS W/O NUTRIENTS
SYSTEM II
INFLUENT
RASCHIG EFFLUENT
CARBON EFFLUENT

FIG. 3


ALKALINITY, mg/l AS $CaCO_3$
o INFLUENT
I. □ RASCHIG FILTER
△ CARBON FILTER
10
20
30
40
50
60
70
80
90
100
1400
1200
1000
800
600
ALKALINITY, mg./l. AS $CaCO_3$
o INFLUENT
II. □ RASCHIG FILTER
△ CARBON FILTER
400
200
000
300

MONTHLY PROGRESS REPORT

FEDERAL HIGHWAY ADMINISTRATION

Date of Report: Dec. 14, 1981

1 Project No.	2 Project Title	3 Report No. 14
FH61-80-C-00111 TECH E20-686	Development of Methodology for the Design and Construction of Stone Columns	From Oct. 1, 1981 To Oct. 31, 1981

4 Research Agency	5 Project Director(s)
Georgia Institute of Technology	Richard D. Barksdale, Director Robert C. Bachus, Co-Director

6 Starting Date	7 Completion Date	8 % Time Expended	9 Schedule Status	10 Sufficiency of Funds
Sept. 1, 1980	Phase I & II Feb. 31, 1982	75%	☐ Ahead ☒ Behind ☐ On	☒ Sufficient ☐ Insufficient

Funds Authorized	Funds Expended		
Total (Phase & II)	13 Total to Date	%	15 Report Month
FHWA $97,800 GaTech $18,300	FHWA: $58,462 GaTech: $3234	60 18	$7,188 (Ga.Tech: $3234)

Project Schedule — Phase II — Time Period (0 1 2 3 4 5 6 7 8)

Research Tasks	% Task Completed
SK A Study	25
SK B sign Methodology	45
rall % pleted	40

Approved Schedule — Work Completed Schedule — Projected Completion Schedule

7 Progress This Month (By Task)

Task A. 1. Begin Test on Rectangular Sample
2. Design Circular Tank

Task B. 1. Continue Finite Element Development of Design Curves and Study Vibroflotation Analysis; Investigate field direct shear test.

Summary of Man-Hours Expended: Task A

	Total	Oct.
1. R.D. Barksdale, Project Director	1158	123
2. R. C. Bachus, Co-Director	834	35
3. Roger Blackwell , Graduate Student	675	69
4. Brent Reid, Student	87	40
5. George Kaffezakis, Graduate Student	60	60
6. Steve Long (Machinist)	70	70
Total:	2884	397

Work Planned for Next Month

1. Continue model tests
2. Continue Finite Element Work
3. Continue evaluation of field direct shear test
4. Continue evaluation of Vibroflotation Co. analysis method

Significant Technical Information, Recommendations, Implementation

None at this time

Problems

None at this time

Report Prepared by

Signature: Dan D Barksdale

Dr. R. D. Barksdale
Name

Project Director
Title

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report
October 1981

by

Edward S. K. Chian
Wendall H. Cross
Frederick G. Pohland
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Stephen R. Harper
Salil Kharkar
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Dr. Leland Paulson

TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from July 1981 through September 30, 1981 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward the initiation of the anaerobic activated carbon filter study and literature search and planning for the pretreatment processes by stripping and solvent extraction methods. The progress of these efforts are depicted in the Gannt Chart (Chart 1) for the above contract, and are presented in detail in the following sections.

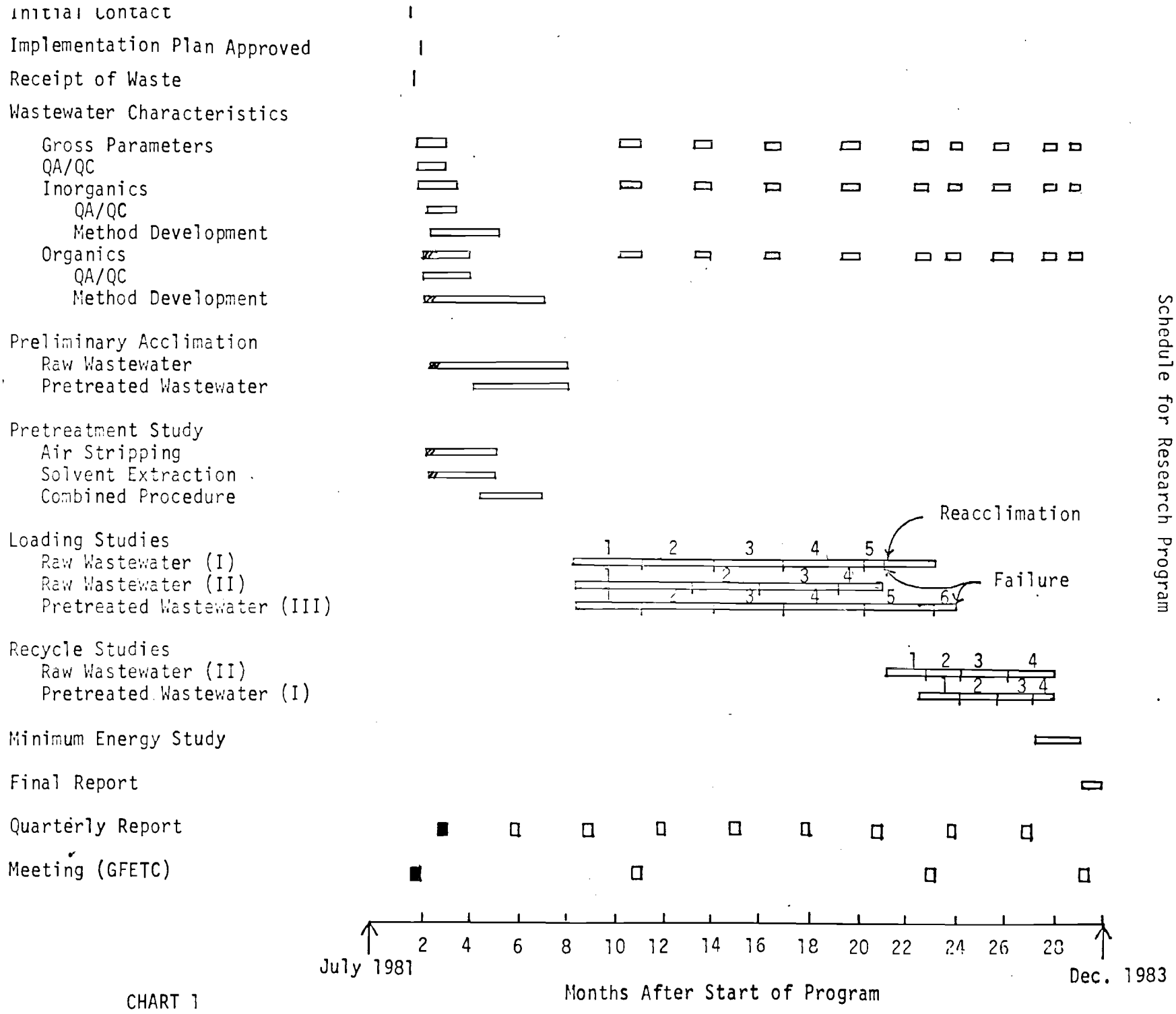


CHART 1

Schedule for Research Program

II. ANAEROBIC ACTIVATED CARBON PROCESS

The primary objectives of the study are to determine and evaluate the overall operating characteristics of the anaerobic treatment systems. These include:

1.) Maximum loading rates for both raw and pretreated coal conversion wastewaters;

2.) Limits of inhibitory or toxic constituent levels in the acceptable raw wastewater;

3.) Levels of pretreatment required to minimize process inhibition or toxicity;

4.) Optimum recycle rates;

5.) Methane generation rates and quantities;

6.) Requirements for nitrification;

7.) Overall process removal efficiencies for organic and inorganic constituent contained in the wastewater; and

8.) Minimum energy requirements for efficient operation.

The above objectives will be met by operating three complete anaerobic and nitrification contact systems in parallel. The use of the three parallel systems will allow for a timely acquisition of data and accomplishment of the research goals.

Since some time will be required for the anaerobic processes to reach steady state, the three systems have been devised to operate concurrently. Systems I and II will be operated on diluted raw coal gasifier wastewater at fixed, but regularly increasing, wastewater loadings and a fixed recycle rate. System I will be operated at slightly higher loadings than System II; as the wastewater loading is increased, System I will thereby be subjected to

possible inhibition or toxicity first. When System I shows signs of failure, System II will still be operating normally and can then be used to determine optimum recycle rates without having to reacclimate the system to the raw gasifier wastewater.

The third system (System III) will be used to determine the degree of pretreatment required prior to use of the wastewater as feed for the anaerobic system. The major constituent to be removed by the pretreatment system will be ammonia. However, pretreatment will not only consist of pH adjustment and air or steam stripping to remove ammonia, but multi-stage solvent extraction to remove cresols, xylenols, phenanthrene, phenols, etc. all coupled with final pH adjustment (to below 7.3) prior to utilization of the pretreated wastewater as feed substrate for the anaerobic treatment system.

Since pretreatment will be employed to reduce the concentration of potentially inhibitory or toxic constituents, System III should be able to accommodate higher wastewater substrate loadings. As with Systems I and II, operating characteristics, e.g., optimum recycle rates, etc., will also be determined for System III.

A. Apparatus

The two-stage anaerobic filter treatment system being used in this study is illustrated in Figures 1 and 2. It consists of an anaerobic roughing filter filled with raschig rings, followed by a filter of equal dimensions filled with granular activated carbon (Filtrasorb 400).

The filter feed system consists of two reservoirs, each equipped with a variable flow rate pump (FMI Model G-150). The pumps feed into a mixing tee which then feeds the filter. The reservoirs contain raw wastewater diluted 1/1 with distilled water and a dilution water containing necessary trace nutrient and buffer which are deficient in the raw wastewater. Therefore,

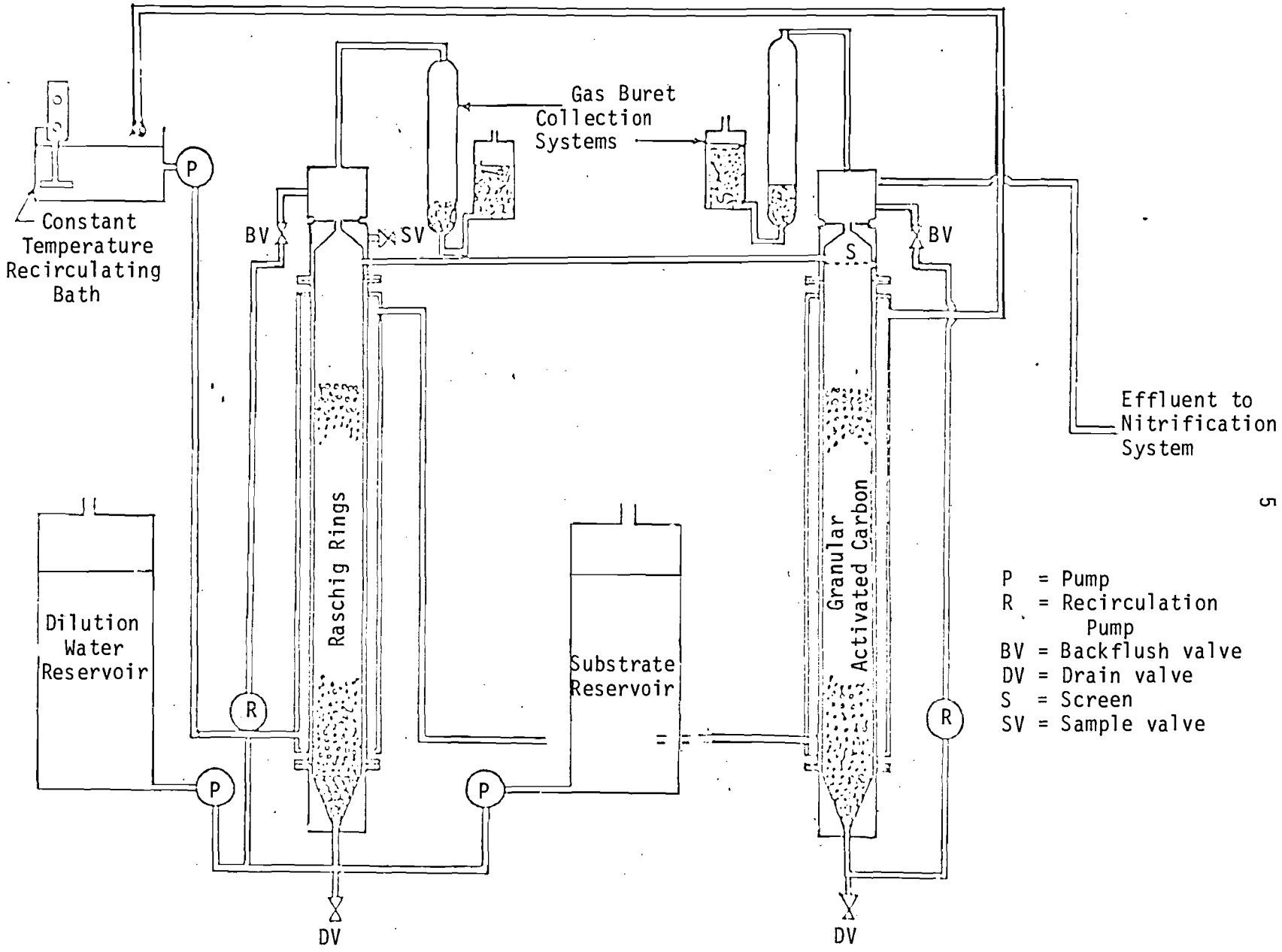


Figure 1 Schematic Diagram of Two-Stage Anaerobic Fixed Bed/Granular Activated Carbon Fluidized Bed Treatment System.

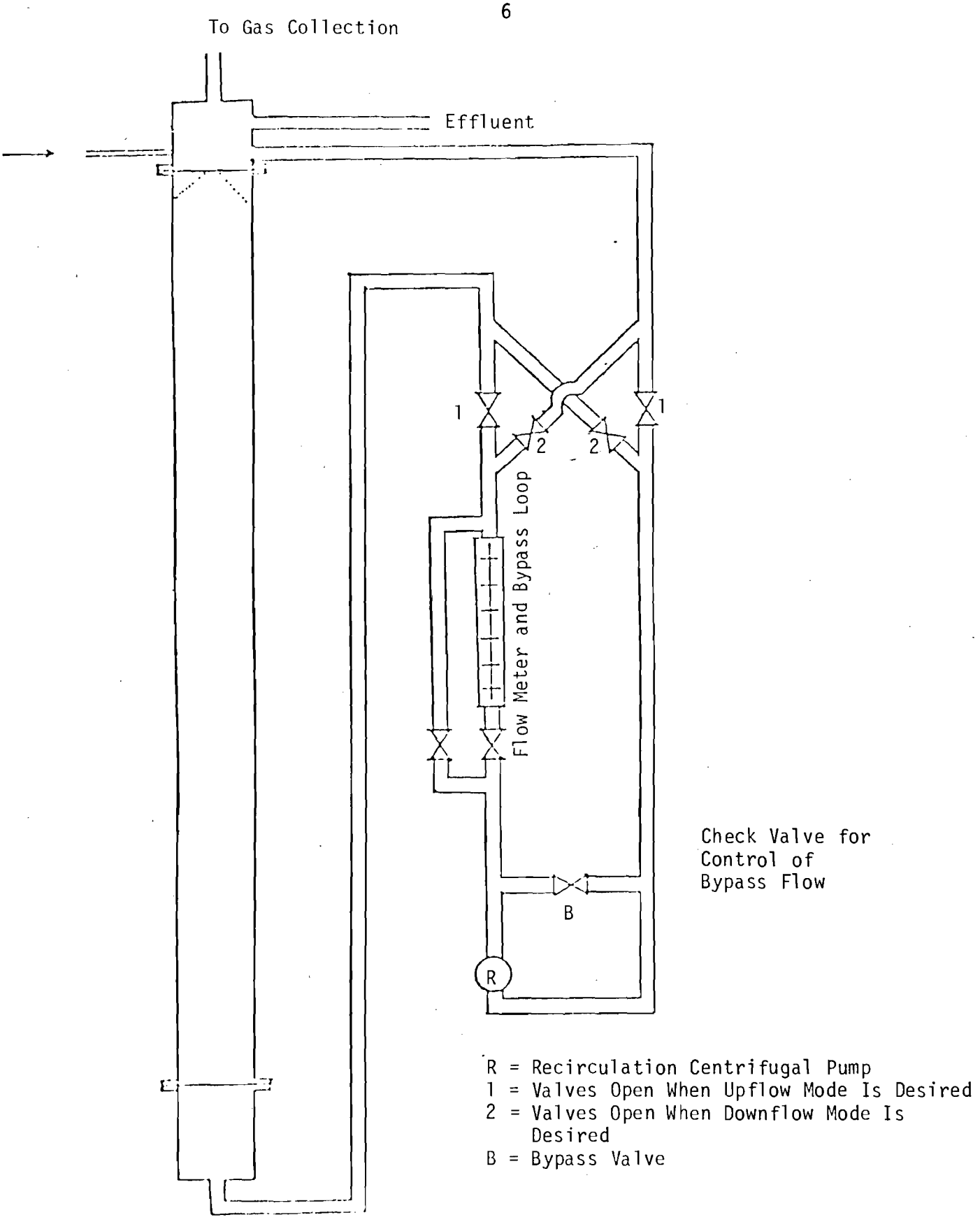


Figure 2 Schematic of Treatment System Effluent Recirculation System

by varying the pump flow rates, it is possible to feed the filter system diluted wastewater of constant composition.

The roughing filter consists of a water jacketed plexiglas column having the following features:

- inner column, 10 cm internal diameter by 183 cm long, packed to a depth of 173 cm with 1.3-cm Raschig Rings;
- influent system, 20 cm long, with an inverted conical shape to allow for better distribution of influent flow and equipped with influent and recycle flow fittings;
- effluent system, 20 cm long, with conical shape to minimize trapped gas volume and equipped with fittings for effluent, recycle, gas collection and sampling;
- gas collection system consisting of two liquid-gas phase separators, two interconnected 4-ℓ gas burets equipped with sampling ports, and two leveling bottles;
- recycle system consisting of a 1/3 h.p. centrifugal pump, flow meter and valves (Figure 2) to allow for either upflow or downflow recirculation of the aqueous contents of the column; and
- thermal water jacket around the main body of each column using 0.64-cm thick, 13 cm diameter cylindrical plexiglas tube. The water jackets are connected in series to the inlet of the recirculating pump of a constant temperature (American Instrument Model No. 4-8600, Silver Spring, Md.). Water is recirculated at a high flow rate through the water jackets in order to maintain a constant and uniform temperature of 35°C $\pm$ 0.5°C.

The anaerobic activated carbon filter is dimensionally identical to the roughing filter except it is packed to a depth of 125 cm with Filtrasorb

"400" granular activated carbon. The pump is utilized to recirculate the aqueous contents and fluidize the carbon bed in order to minimize gas entrainment and provide internal buffering and dilution of the column influent. The activated carbon columns also have an additional expansion chamber at the effluent to allow for settling of carbon fines. This chamber is 30 cm long and 15 cm in diameter.

B. Feed Solutions.

Raw wastewater from the Grand Forks Energy Technology Center, North Dakota, is stored at -15°C until use. The raw wastewater, which contains approximately 10,000-12,000 mg/L TOC, is diluted 1/1 with distilled water. Glucose is then added as a carbon source to help acclimate the seed organisms to the gasification wastewater. The influent is then diluted 9 to 1 with diluent buffer solution before being fed to the roughing filter.

It is anticipated that an organic carbon loading of 1000 mg/L will be suitable for microorganism acclimation. Presently, half of this TOC load is made up of glucose. The wastewater currently being fed into the treatment system contains approximately 4800 mg/L TOC from glucose and 5200 mg/L TOC from the gasifier effluent. As acclimation progresses, the glucose feedings will be reduced and the wastewater will eventually serve as the only carbon source for the anaerobic culture.

The 1/2-strength wastewater will be diluted, buffered and fortified with nutrients by the dilution buffer solution. Each liter of diluent contains the ingredients listed in Table I.

C. Process Performance Monitoring

Presently, the treatment systems are still in the process of acclimation. Therefore, extensive chemical analyses are presently not being routinely performed. However, daily checks of pump flowrates, reservoir volumes, pH,

TABLE I. Concentration of Ingredients in Dilution Water

Ingredient	Concentration
KH_2PO_4, mg/L	0.68
$NaH_2PO_4 \cdot H_2O$, mg/L	0.69
5N KOH + 5N NaOH solution, ml/L	5
Vitamin Extract*, ml/L	4

*The vitamin extract was prepared by adding 10 grams of a multivitamin to 333 ml of 95% ethanol and 667 ml of distilled water. The solution was allowed to stir for 10-12 hours at 60°C, settled for 24 hours and decanted for use.

and gas production are recorded. In addition, weekly tests for TOC, COD, and gas composition have been initiated.

System response will continue to be observed and, as soon as a pseudo steady-state operation is achieved (as determined by constant gas production rates and a constant COD conversion), intensive analysis of the influents and effluents to and from each unit will be made in order to assess the performance of the unit not only in terms of overall efficiency but also in terms of the removal of specific constituent from the wastewater. The initial research plan for parameters to be analyzed are listed in Table 2. This plan may be modified as first results are analyzed to determine treatment trends, and possible additional sampling may be indicated. The present schedule calls for the following.

pH. The pH of the influent and effluent are measured immediately after sample withdrawal using a Fisher Accumet pH Meter, Model 144 (Pittsburgh, Pa.).

Total Inorganic and Organic Carbon. The total inorganic carbon (TIC) and total carbon (TC) contents of the influent substrate and effluents from

Table 2

Parameter Analyzed	Raw Wastewater	Diluted Raw Wastewater	Roughing Filter Effluent	Carbon Filter Effluent
COD	+	+	+	+
TOC/TIC	+	+	+	+
NH_3	+	+		
pH	+	+	+	+
CN^-	+	+		
SCN^-	+	+		
Alkalinity	+			+
Volatile Organic Acids	+		+	+
ORP			+	+
Specific Organics	+			+
	+			+
	+			+
	+			+
	+			+
Metals	+			+
	+			+

Gas Production and Composition will be obtained for both the roughing filter and the carbon filter.

all columns are measured using a Beckman Model 915 Total Organic Carbon Analyzer (Fullerton, CA). All samples will be filtered through 0.45-μm Gelman Metricel membrane filters (Ann Arbor, Mich.) prior to analysis. The total organic carbon (TOC) content of the samples is determined as the difference between the TC and TIC.

Chemical Oxygen Demand. The COD present in the feed and effluents from all columns is determined by the COD test as described in Section 508 of Standard Methods for the Examination of Water and Wastewater[1]. All samples are filtered through a 0.45-μm Gelman Metricel membrane filter prior to the analysis.

Alkalinity. Total alkalinity determinations are performed on all influent and column effluent samples according to the procedure described in Section 403 of Standard Methods for the Examination of Water and Wastewater.[1]

Ammonia Nitrogen. Ammonia nitrogen determinations are performed on filtered samples using the Technicon Corporation Industrial Method 19-69W (Tarrytown, NY). The automated procedure for the determination of ammonia in water using the Technicon AutoAnalyzer Proportioning Pump in conjunction with a Technicon AutoAnalyzer Sampler and Recorder utilizes the Berthelot reaction in which the formation of a flue-indophenol complex occurs when the ammonium bearing solution is added to sodium phenoxide followed by the addition of sodium hypochlorite. A solution of potassium sodium tartarate (Rochelle Salts) is added to the sample stream to eliminate the precipitation of the hydroxides of any heavy metals which may be present.

Gas Analysis. Gas samples are being analyzed for methane, carbon dioxide, nitrogen and oxygen using a Fisher Gas Partitioner Model 25V (Pittsburgh, PA) in conjunction with a Fisher Thermal Stabilizer Model 27 and a Coleman Recorder, Hitachi 165 (Pittsburgh, PA).

Phenol Determination. Phenol concentrations will be determined using one of the three methods: a) UV-absorption, b) GC-analysis, c) 4-Aminoantipyrene method.

Oxidation Reduction Potential. A 70-ml continuous flow-through cell having three ports was designed for the measurement of the in situ oxidation reduction potential (ORP). A platinum combination electrode connected to a Fisher Accumet pH Meter, Model 144, will be inserted tightly in the continuous flow cell. The other two parts of the cell will be connected to the two tee connections on the recirculation line of the column under consideration. The flow-through cell will be filled slowly in an upright manner to avoid an oxygen contamination; once filled and sealed, the recirculated flow will be completely diverted through the cell and ORP recorded when the reading has stabilized. All ORP values will be reported versus a saturated calomel reference electrode.

Specific Organics. An analytical methodology which consists of solvent extraction, liquid chromatography fractionation and final assessment by High Resolution Gas Chromatography - Low Resolution Mass Spectrometry - Data System (HRGC-LRMS-DS) will be employed for the preliminary characterization of specific organic compounds present in the coal conversion wastewater. As soon as the anaerobic activated carbon process reaches a pseudo steady state operation, the effluent will be monitored and the organic components quantitated according to the analytical methodology thus established. A QA/QC for the analytical methodology will be implemented during the monitoring phase.

Data Report. Data for the aforementioned analyses will be logged using the following forms (Fig. 3-6). The roughing filter effluents are designated by an R and the activated carbon filters by the letter A. The six columns involved in the study are therefore 1R, 1A, 2R, 2A, 3R and 3A.

Fig. 3

TIME	INITIAL	GAS PRODUCTION, ml. -per buret - reading/reset							
		1/reset	2/reset	3/reset	4/reset	5/reset	6/reset	7/reset	8/reset

Fig. 4

E	TIME	INITIAL	pH							ALKALINITY, mg/1. as $CaCO_3$						
			INLUENT	EFFLUENT FROM COLUMN						INFLUENT	EFFLUENT FROM COLUMN					
				1R	1A	2R	2A	3R	3A		1R	1A	2R	2A	3R	3A

Fig. 5

TIME	INITIAL	TOC, mg/1.							COD, mg/1.						
		INLUENT	EFFLUENT FROM COLUMN						INFLUENT	EFFLUENT FROM COLUMN					
			1R	1A	2R	2A	3R	3A		1R	1A	2R	2A	3R	3A

Fig. 6

'IME	INITIAL	INORGANICS: INFLUENT/EFFLUENT, mg/1.					
		CN^-	SCN	$S^=$	NO_2	NO_3	NH_3

D. Start Up and Acclimation

In order to establish the needed anaerobic microbial culture, filters 1R and 2R were filled with a mixture of municipal anaerobic sludge and process water from the anaerobic digestion of a phenol substrate. The municipal sludge was obtained from Atlanta's R. M. Clayton Wastewater Treatment Plant. The phenolic wastewater was obtained from an ongoing study at Georgia Institute of Technology. Systems I and II are currently being fed a 20/1 dilution of the raw wastewater, which is supplemented with nutrients and glucose as described earlier. Initial gas production volumes for filters 1R, 1A, 2R, and 2A are given in Table 3.

The variability in gas production rates is due to a number of factors. The primary factor has been feed pump failures and feed system modifications. Initially, each of the three systems were fed from individual reservoirs. This approach was abandoned in favor of central reservoirs for both the raw wastewater and the diluent buffer. These new reservoirs are 200-liter polyethelene drums, and each feeds all the systems simultaneously. This approach will also aid in maintaining a relatively consistent influent, as the reservoirs will be kept "topped up", rather than periodically refilled with large batch solutions. The variability from batch to batch in the former approach may have also accounted for some of these variations. The gas collection system has also been closely inspected and repaired as needed. With these changes implemented, gas production rates should start to show a more consistent trend.

Most of the operational problems are under control, and weekly monitoring of pH, alkalinity, TOC and COD should begin by Oct. 20.

TABLE 3

Gas Volumes Produced, ml/day

DATE	COLUMN			
	1R	1A	2R	2A
10/06/81	130	0	0	0
10/07/81	4100	0	130	0
10/08/81	-	0	-	400
10/09/81	3300	0	1100	300
10/10/81	2200	0	-	2800
10/11/81	4300	0	600	600
10/12/81	3050	0	0	500
10/13/81	200	0	0	2150

E. Future Work

The phase of the project following acclimation will consist of changing the raw wastewater - dilution water ratio for System I to a value of 2 to 8 in order to increase the loading on System I. The loading on System II will remain at 1:9 ratio. As soon as pseudo steady-state conditions are achieved, System I performance will once again be evaluated in the same manner as before. Following this evaluation, the raw wastewater-dilution water ratio for the feed to System I will be changed and that for System II will also be changed. Again, pseudo steady-state operation will be allowed to be established and the performance of System I will be evaluated.

Systems I and II will continue to be operated in this fashion (with System II always being one loading step behind System I) until System I either exhibits poorer performance due to inhibition or fails due to toxicity. At that time, System II can be utilized to assess the effect of recycle rate on system performance, since it will not have been operated at inhibitory or toxic concentrations of wastewater constituents. Recycle rates will be varied over a range of 10 to 50% bed expansion in order to determine optimum values of bed expansion which will minimize energy input to the system for operation while giving a maximum gas productions.

System III will be operated in a similar manner to Systems I and II except pretreated wastewater will be used as feed substrate instead of the raw wastewater. Pretreatment by stripping and solvent (MIBK) extraction will be monitored for removal of NH_3, COD and TOC, as well as cresols, xylenols, phenols, phenanthrene, methyl naphthalene, dimethyl naphthalene, biphenyls, etc.

System III performance will be evaluated in a manner analogous to Systems I and II. It is anticipated that System III will be able to operate at lower dilution ratios than System I and II due to the removal of potentially inhibitory

or toxic materials in the pretreatment process. Therefore, only a simple unit will be used for this part of the study. Once maximum loading rates are determined for System III, the optimum recycle rates for most efficient operations will be determined.

The principle anticipated difficulty in the operations of the treatment systems is in allowing sufficient time for pseudo steady-state operating conditions to be obtained. It is anticipated that two to three months will be required for reaching acceptable steady state during each phase of the project, including loading and recycle changes, respectively.

Special attention also will be given to the proposed nitrification system. Since the anaerobic process should produce sufficient alkalinity for nitrification to occur, direct nitrification of the effluent from the anaerobic processes will be examined. However, if alkalinity is not sufficient to allow for complete nitrification, feed substrate to the nitrification systems will be supplemented as required to allow nitrification to proceed efficiently. A completely mixed nitrification activated sludge system followed by a final clarifier will serve to polish the effluent. The aeration basin to be used is equipped with an adjustable effluent port to allow changes in hydraulic detention times in the basin. The clarifier is equipped with both sludge recycle and sludge wastage pumps to allow for recycle of biomass to the aeration basin and for wastage of any excess biomass produced, respectively.

III. PRETREATMENT PROCESSES

The effort for the pretreatment process evaluation will be focussed on two major parts. i) solvent extraction in order to decrease the total organic content of the wastewater and to remove potential toxic and/or inhibitory compounds; ii) stripping methods in order to decrease the amount of ammonia and other dissolved gases.

The efficiency and the appropriate sequence of the above processes will be investigated on a laboratory scale. In addition some effort will be devoted to make a workable physico-chemical process which will allow for solvent and ammonia recovery and would prove feasible economically when scaled-up to a pilot plant dimensions.

A. Solvent Extraction

Solvent extraction will be utilized primarily for the removal of toxic and/or inhibitory organic compounds, which could interfer with the anaerobic biological treatment processes, and consequently lower the efficiency of treatment.

Solvents which have been evaluated [2] for the removal of phenolics include tricresyl phosphate, n-butyl acetate (NBA), Di-isopropyl ether (DIPE), methyl-isobutyl ketone (MIBK) and light oil comprised of benzene, toluene and xylene. Desirable solvent properties include relatively low aqueous solubility and high partition coefficients for organic compounds.

According to the available literature [2-6], MIBK is considered the most promising solvent and will be extensively evaluated.

In order to evaluate the solvent extraction process, model organic compounds will be selected and monitored. The selection criteria will be based on two factors: i) the presence and concentration of the compound in the wastewater; and, ii) their specific acid and base, polar and non-polar character.

According to the literature sources [3-5], the main parameters that would

affect the process are: i) temperature, ii) pH, iii) time and intensity of mixing (for a batch process), and iv) concentration of the model compounds. In our investigation, temperature, pH and the degree and intensity of mixing will be held constant and the concentration of the model compounds shall be the only variable parameter. At least four different concentration will be evaluated that are included within the concentration range of 5.0 to 5000 mg/l.

The partition coefficient is defined as follows:

$$K_D = \frac{C_s}{C_w} = \frac{(W_o - W_i)\ /V_s}{W_i/V_w}$$

where;

K_D = partition coefficient

C_s = concentration of the model compound in solvent, mg/l

C_w = concentration of the model compound in water, mg/l

W_o = initial weight of model compound in water, mg

W_i = final weight of model compound in water, mg

V_s = volume of solvent, l

V_w = volume of water, l

The batch extraction will be utilized for the evaluation of K_D[7]. Equal volumes of solvent and "organic free" distilled water fortified with a known amount of the model compounds will be brought into contact, and 20 minutes each will be allowed for mixing and settling. Most of the solvent will be decanted, and a separatory funnel will be used to remove the remainder of the solvent.

As indicated by the partition coefficient relation, the only unknown to be experimentally evaluated is the final concentration of the model compound in water. An analytical method will then be established, which will involve solvent extraction of the separated water at pH 2 and pH 12, organic solvent concentration by Kuderna-Danish (K-D) apparatus and instrumental analysis by gas-

chromatography and flame ionization detector (GC-FID).

Methylene chloride will be utilized as the solvent extractor for the analytical methodology. A quality assurance/quality control program (QA/QC) will be implemented as soon as the analytical methodology has been established. Precision and accuracy will be expressed as standard deviation (S) and arithmetic mean ($\bar{X}$), respectively.

An optional configuration of multistage counterflow extraction process will be found.

B. Ammonia Removal

Various methods have been established for the removal of ammonia from wastewater[2,8,9]. Removal of ammonia by ion exchange uses the selective affinity of clinoptilolite, a natural zeolite, for ammonia ion in solution. This resin can be regenerated at high pH with sodium or calcium salts, air stripped to remove ammonia, and recycled. However, the presence of organic material, such as is in gasification wastewaters, will significantly retard the effectiveness and useful life of the resin[8]. A recent study comparing ion exchange versus steam stripping for ammonia removal concluded that, on the basis of investment and operating costs, the ion exchange process is not competitive economically with a stripping system[10].

Breakpoint chlorination for converting ammonia to nitrogen gas may be a viable alternative only when treating wastewater streams that are relatively low in ammonia content. Also, chlorine demand is exerted by S^{-2}, HS^{-}, SO_3^{-2}, CN^{-1}, NO_2^{-2}, Fe^{+2}, hydroxybenzenes and amino acids, most of which are found in gasification wastewaters. The increased chloride used, over and avobe that necessary for ammonia removal, will increase the total dissolved solids content of the treated wastewater[11], involve high operating costs[11] and most important, will prove toxic to the subsequent anaerobic biological system.

At this stage of the project, the following two options are the most promising:

1) air stripping; or, 2) steam stripping of ammonia both with or without chemical addition for pH adjustment. Both these options will be evaluated to determine the most economical and practical approach.

In the pH range of 8.2 to 9.0 that the wastewater exhibits, the percentage distribution of ammonia and ammonium ion at 25°C, is 10% ammonia and 90% ammonium ion[12]. The stripping of ammonia from wastewater involves two steps: i) conversion of ammonium ion to ammonia; and, ii) removal of ammonia from the wastewater.

At a pH above 7 the equilibrium in the reaction

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

is shifted to the right. With an alkalinity greater than 10,000 mg/l as $CaCO_3$, at a pH = 8.5 in the wastewater providing sufficient buffering capacity, an attempt will be made to utilize this property for the reduction in the ammonia concentration to about 500 mg/l without having to resort to chemical addition.

Experiments by Luthy[2] have indicated that it is possible to achieve up to 90% ammonia removal with this wastewater without having to adjust the pH. Scaling[13] being the most prevalent problem associated with lime addition, as also solids production, the reduction of ammonia concentration without chemical addition is justified. Chemical addition will, however, be resorted to for further reduction in ammonia concentration to less than 100 mg/l if deemed necessary.

Of the two options stated earlier, air stripping of ammonia will be attempted first. The complex nature of the wastewater warrants batch tests to be carried out to determine the amount of ammonia that can be removed without any chemical addition, and the amount of chemicals required to achieve ammonia removal to concentrations of less than 100 mg/l.

Based on the results of the test, an attempt will be made to design and fabricate a countercurrent type air stripping tower, packed with raschig rings

for continuous treatment of the wastewater.

Additional benefits of stripping is the reduction in alkalinity and sulphide concentrations in the wastewater[2]. The total carbon and total organic carbon concentrations will be closely monitored to determine whether any volatile organics are also being stripped from the wastewater.

Both solvent extraction[3,4,5,7] and ammonia stripping[12,13] being pH dependent processes, the sequence of their operation will be carefully evaluated for maximum efficiency of removal.

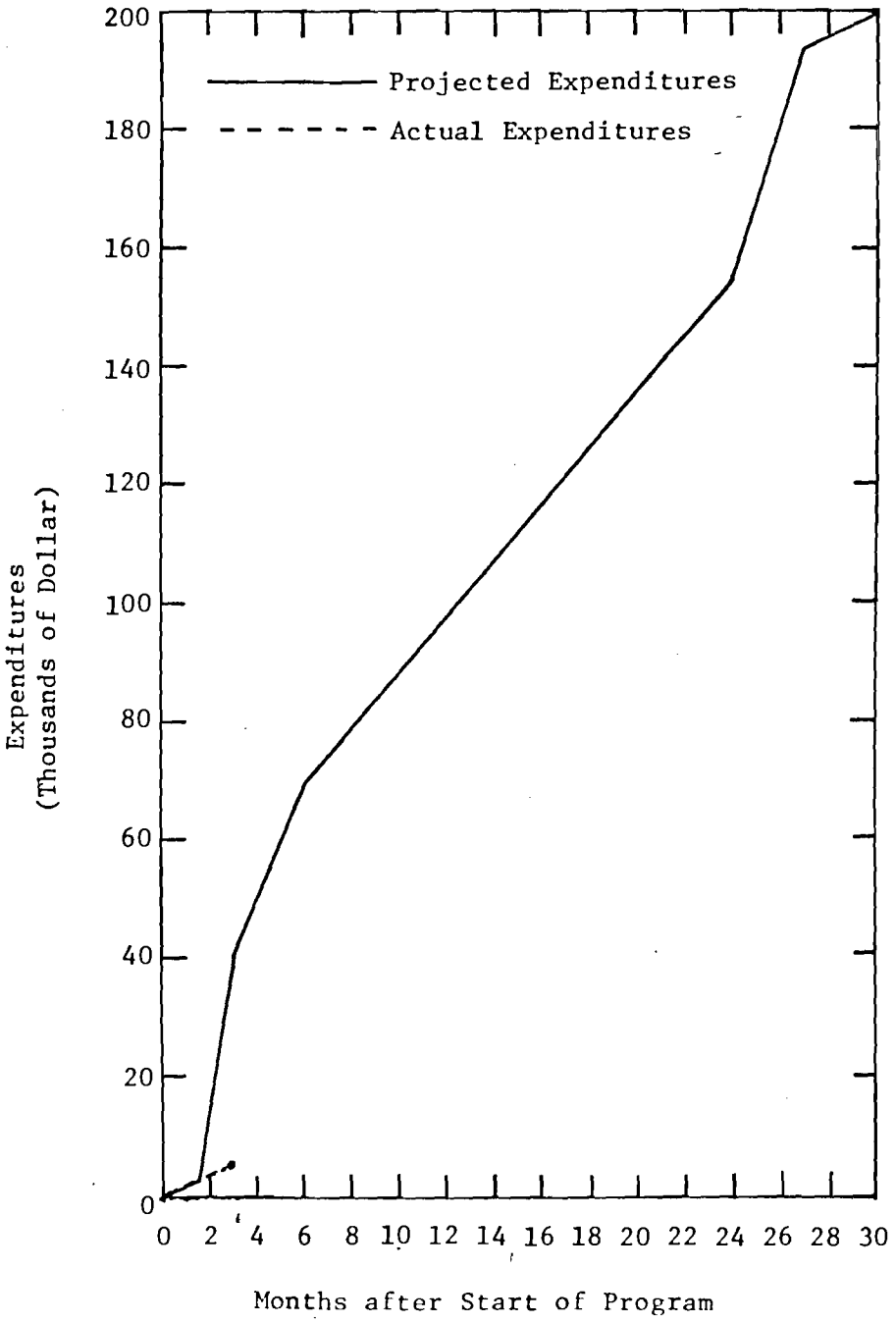
IV. FUTURE WORK

Attempt has been made in this report to include future work of this research program at the end of each section.

V. EXPENDITURES

The actual expenditures incurred during the first quarter of this research program are presented by the dashed line in Figure 1 (between months of 0-3). The solid line represents the expected expenditures in the months to come.

Fig. 7



Projected Expenditures for DOE Contract
No. DE-AC18-81FC10297

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I. INTRODUCTION

This report summarizes the work performed during the period from October 1, 1981 through December 30, 1981 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward the continued acclimation of two anaerobic treatment systems, start up of a third anaerobic treatment system, GC/MS characterization of the coal gasification wastewater, data aquisition for determination of distribution coefficients for the extraction of phenol from the wastewater using MIBK, and preliminary design of a solvent extraction system for wastewater pretreatment. The progress of these efforts are depicted in the Gannt Chart (Figure 1) along with project expenditures for the above contract, (Figure 2) and are presented in detail in the following sections.

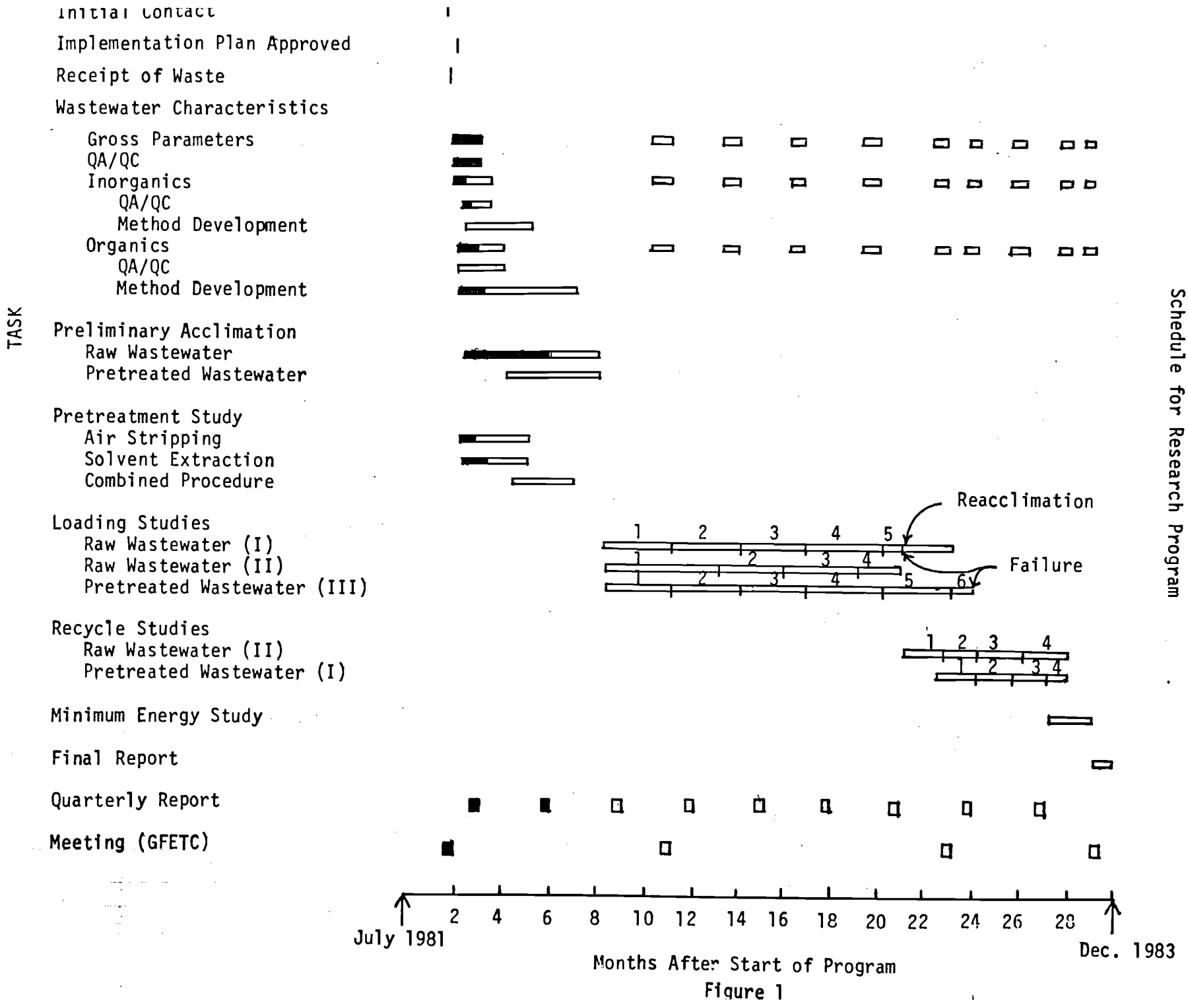
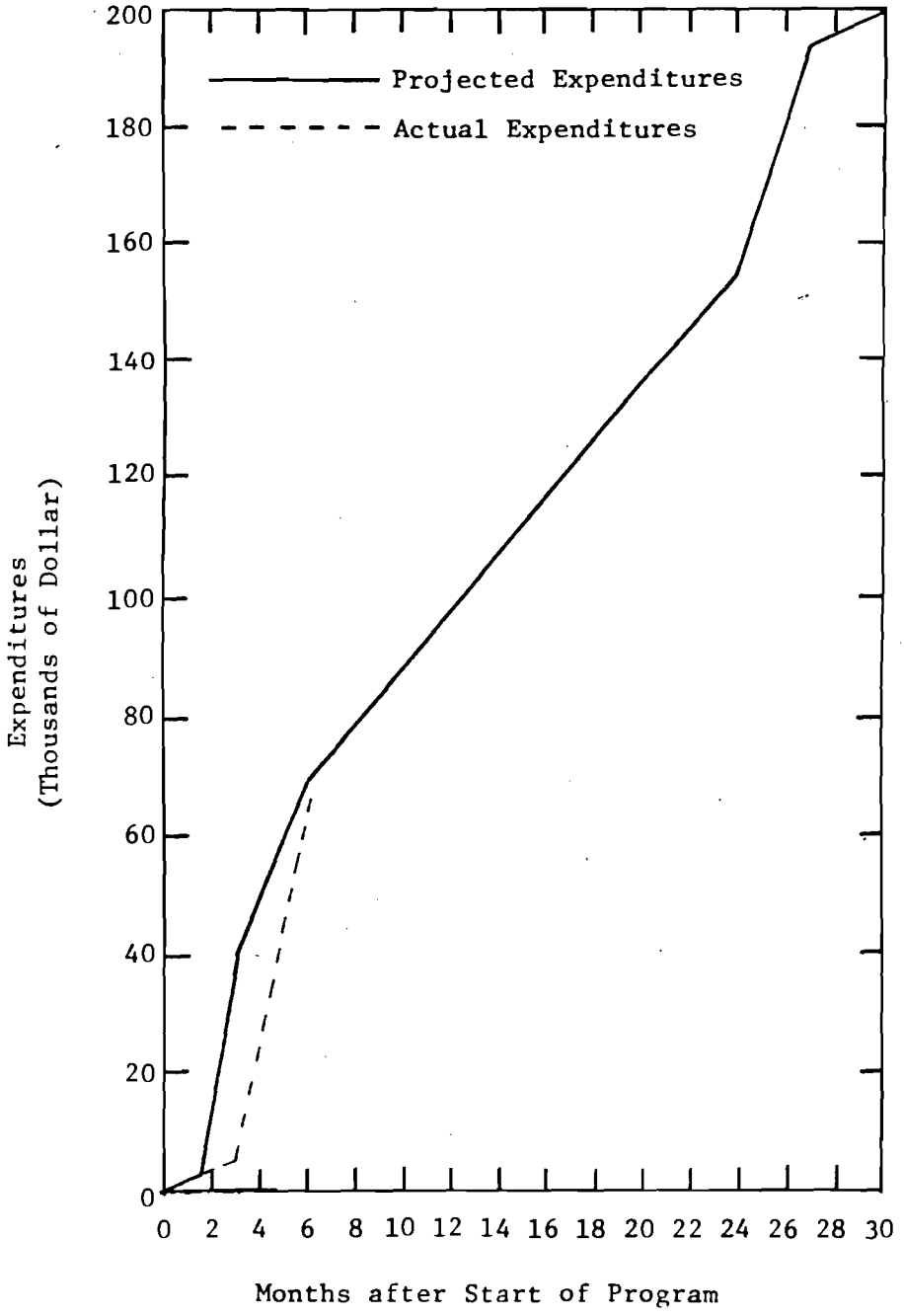

TASK
Initial Contact
Implementation Plan Approved
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
Method Development
Preliminary Acclimation
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
July 1981
Dec. 1983
Months After Start of Program
Schedule for Research Program

Figure 1



Projected Expenditures for DOE Contract
No. DE-AC18-81FC10297

Figure 2

II. ANAEROBIC TREATMENT SYSTEMS

A. Systems I and II

1. Operation and Acclimation

System I and II have been initially operated in an identical fashion for a period of 70 days. Diluted wastewater containing glucose, phospates and vitamin extract (Table I) was pumped through the columns at a flow rate of 10 ml/min. At the end of 25 days the addition of vitamin extract to the dilution water was discontinued. At the end of 50 days the glucose supplement was discontinued. After an additional ten days of operation the activity within the reactors was decreasing as evidenced by both reduced gas production and a decrease in total volatile acids within the systems. It was decided to supplement the feed to one system with a low level of glucose. Therefore, on day 60 of operation, glucose, equivalent to 300 mg/l TOC, was added to the feed of System II. Simultaneously the flow rate to the Rashig Ring columns of both systems was reduced to 6.7 ml/min. The effluent from the Rashig Ring column was combined with an additional flow of 3.3 ml/min of final effluent from an anaerobic system being operated on phenol prior to being pumped through the granular activated carbon columns. This anaerobic effluent contains only a low residual COD of 40 mg/l, zero phenol and active methanogenic organisms. The results of these changes in operation will allow for the evaluation of two means of acclimation; that is acclimation by supplementation with an easily degraded substrate versus acclimation using diluted raw wastewater alone.

2. Volatile Acid Production

Both systems are producing volatile acids with the overall concentrations being similar in both systems (Figures 3 and 4). The concentration of acids in the final effluent of System I is higher which is also reflected by a lower gas production in System I, indicating that an active methane producing population of microorganisms has not been established in System I.

TABLE I. Feed Solution For System I and II

Days of Operation	Feed Solution
0-25	Raw Wastewater (500 ppm TOC), Glucose (500 ppm TOC), Phosphates, Vitamin Extract
25-50	Raw Wastewater (500 ppm TOC), Glucose (500 ppm TOC), Phosphates
50-70	Raw Wastewater (800 ppm TOC), Phosphates
70-75	System I - Raw Wastewater (800 ppm TOC), Phosphates System II- Raw Wastewater (700 ppm TOC), Glucose (300 ppm TOC), Phosphates
75-present	Same as days 70-75 except diluted wastewater flow rate was reduced to 6.7 ml/min and an additional 3.3 ml/min of effluent from an operating phenol degradation unit was pumped through the GAC column

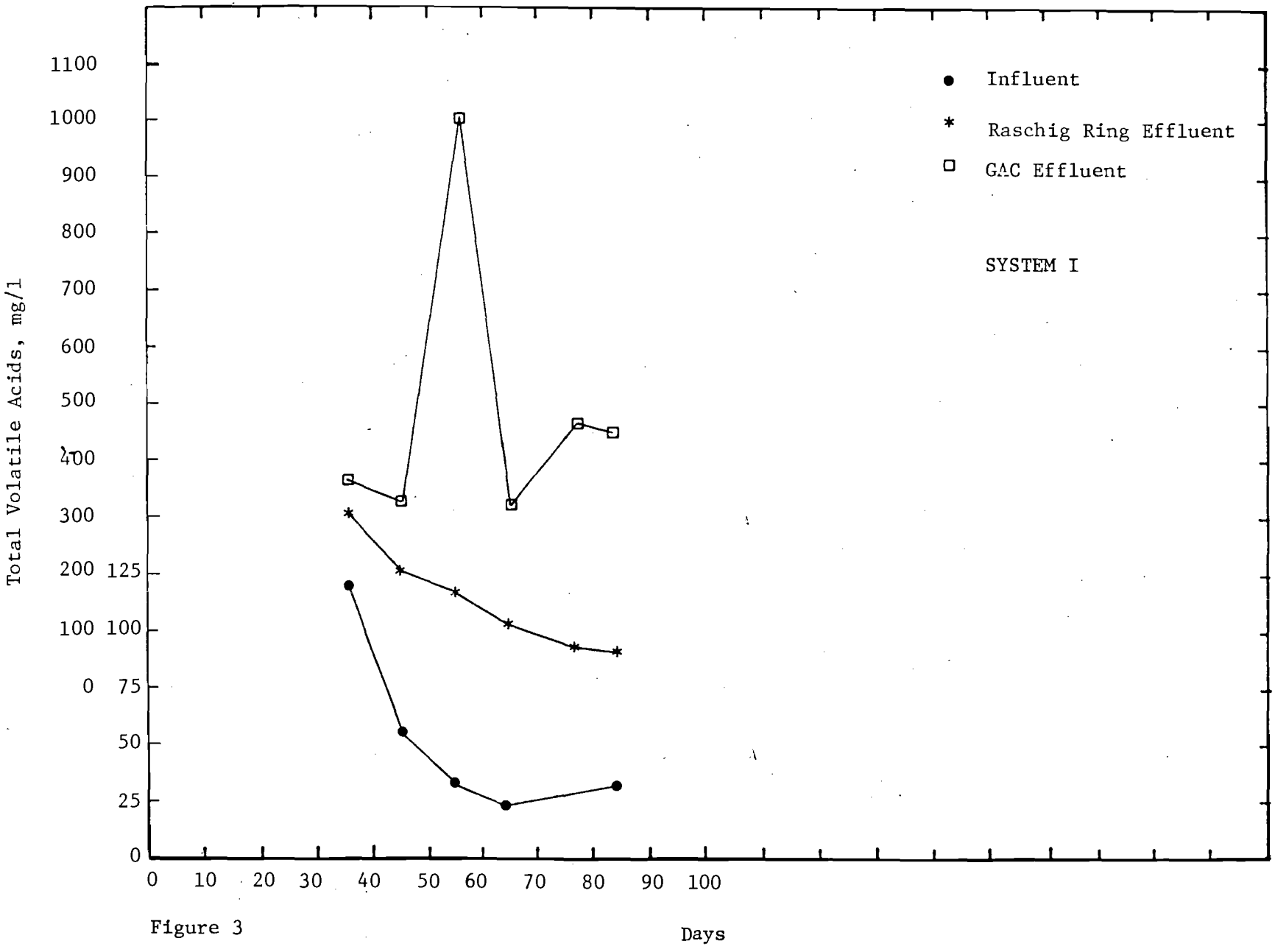

Total Volatile Acids, mg/l
1100
1000
900
800
700
600
500
400
300
200
125
100
100
0
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100
Days
Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM I

Figure 3

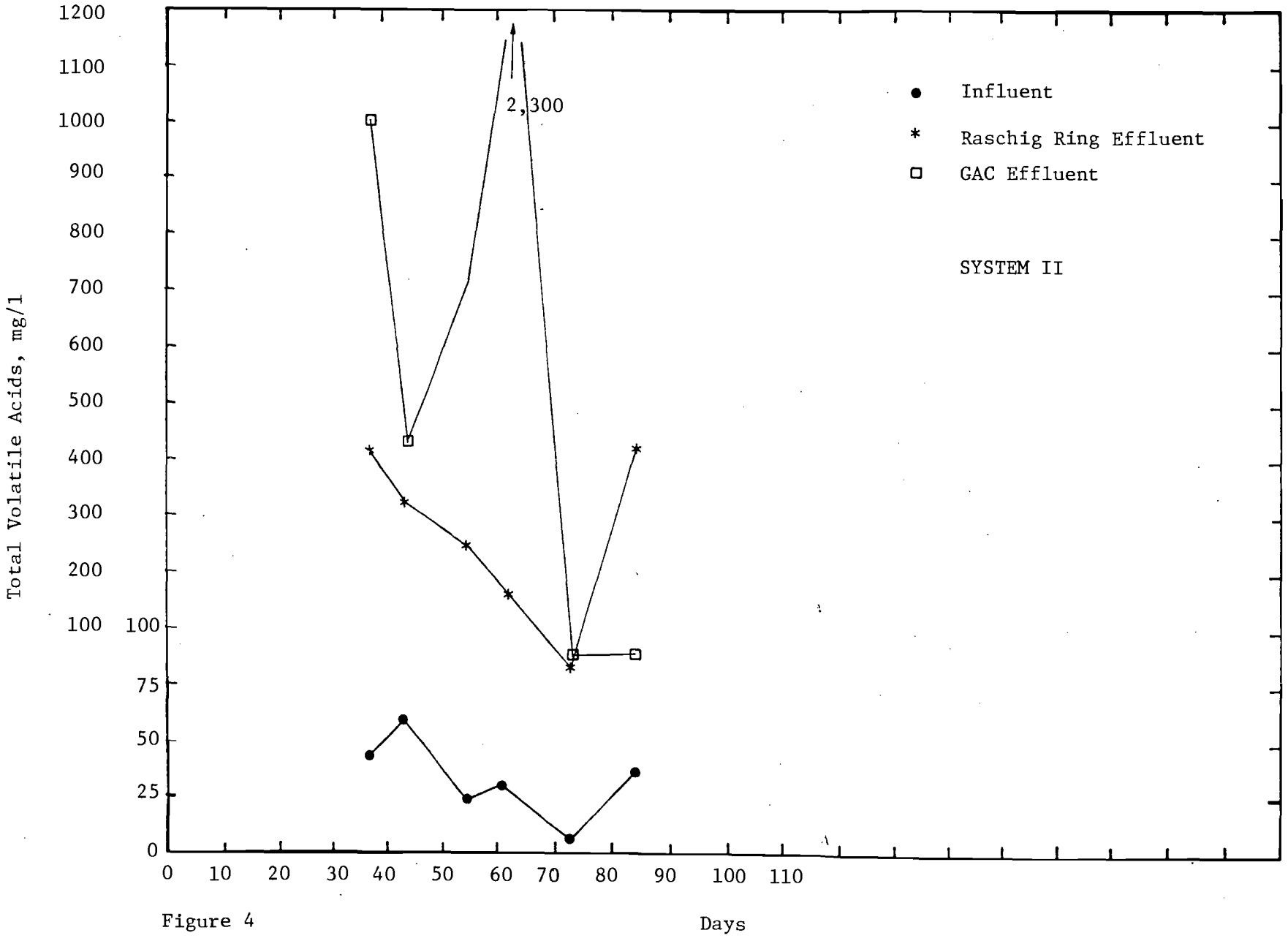

Total Volatile Acids, mg/l
1200
1100
1000
900
800
700
600
500
400
300
200
100
100
75
50
25
0
0
10
20
30
40
50
60
70
80
90
100
110
Days
2,300
Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM II

Figure 4

Concentrations of volatile acids in the effluent from the Raschig Ring Columns in both systems are increasing indicating that viable acid forming populations of microorganisms are being established in the Raschig Ring Columns of both systems.

3. Gas Production

Both System I and II are producing measurable quantities of methane rich gas (Figure 5). Average methane content is 60 to 70%. As can be seen by Figure 5 both systems were producing at a relatively constant rates until shortly after the glucose supplement was discontinued (day 50 of operation). The gas production rate then decreased rather markedly, therefore, one system received an additional glucose supplement at a level of 300 mg TOC glucose to ascertain if this process would shorten the required acclimation time for the system. As can be seen in Figure 5 the addition of glucose has markedly increased the gas production rate in System II. The increase in the quantity of gas produced is more than can be accounted for by complete conversion of the added glucose to methane and carbon dioxide. Therefore, it is concluded that the system is anaerobically converting some of the organic compounds in the raw wastewater to methane and carbon dioxide. The bulk of the gas currently being produced in System II is being produced in the GAC column.

System I is still producing measurable quantities of gas in both the Rashig Ring and GAC columns but at a much lower rate than System II.

4. Phenol Removal

Phenol removal is occurring in both systems (Figure 6 and 7). Increases in phenol concentration in the final effluent are indicative of saturation of the GAC with incomplete biodegradation of the phenol occurring at this time. Phenol removal efficiencies should improve as acclimation proceeds.

5. COD and TOC removals

Influent COD and TOC (Figures 8,9,10,11) values are becoming more uniform indicating improvements in method of substrate preparation. Overall removals are similar in both systems at this time and are expected to improve as acclimation proceeds.

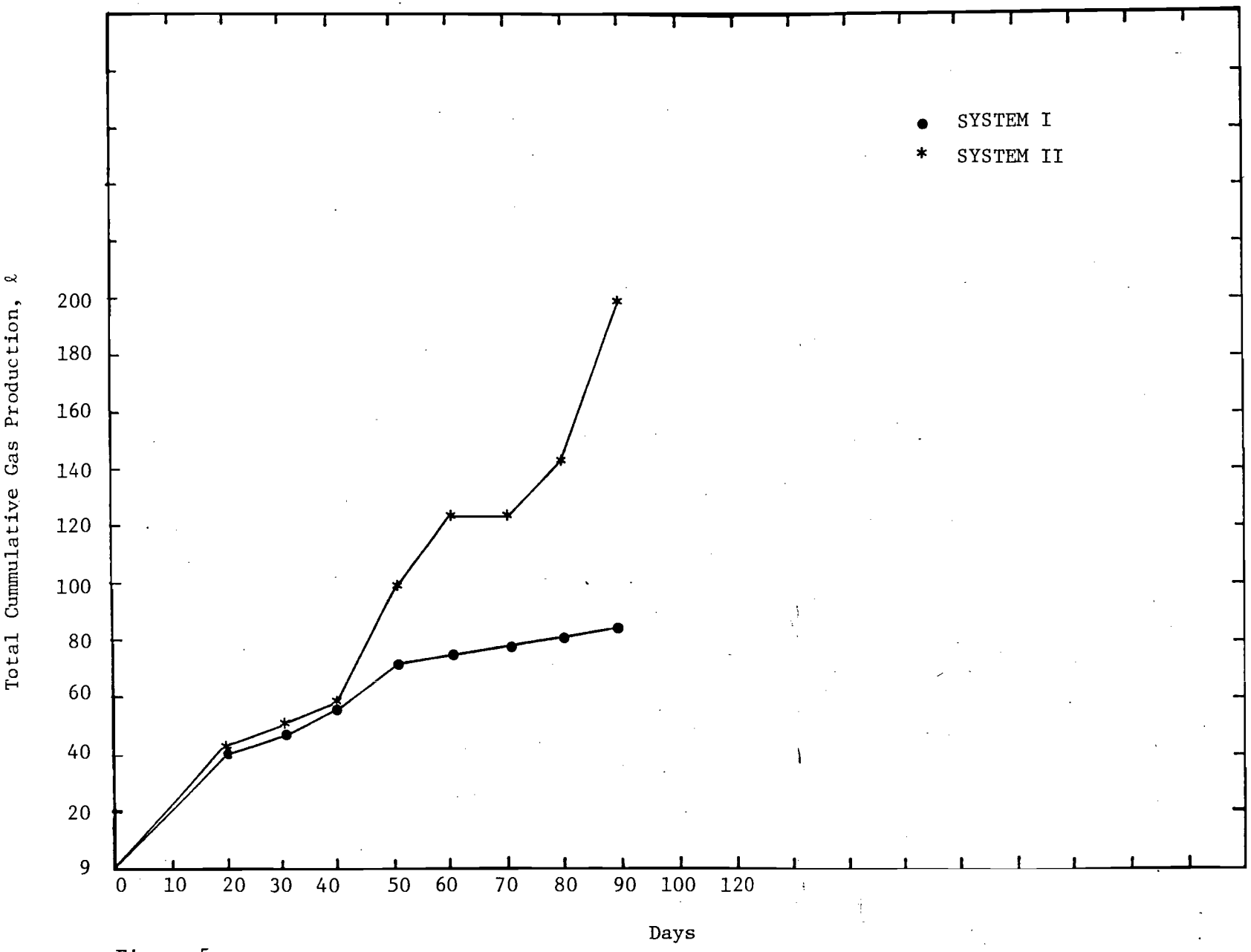

SYSTEM I
SYSTEM II
Total Cummulative Gas Production, ℓ
200
180
160
140
120
100
80
60
40
20
9
0
10
20
30
40
50
60
70
80
90
100
120
Days

Figure 5

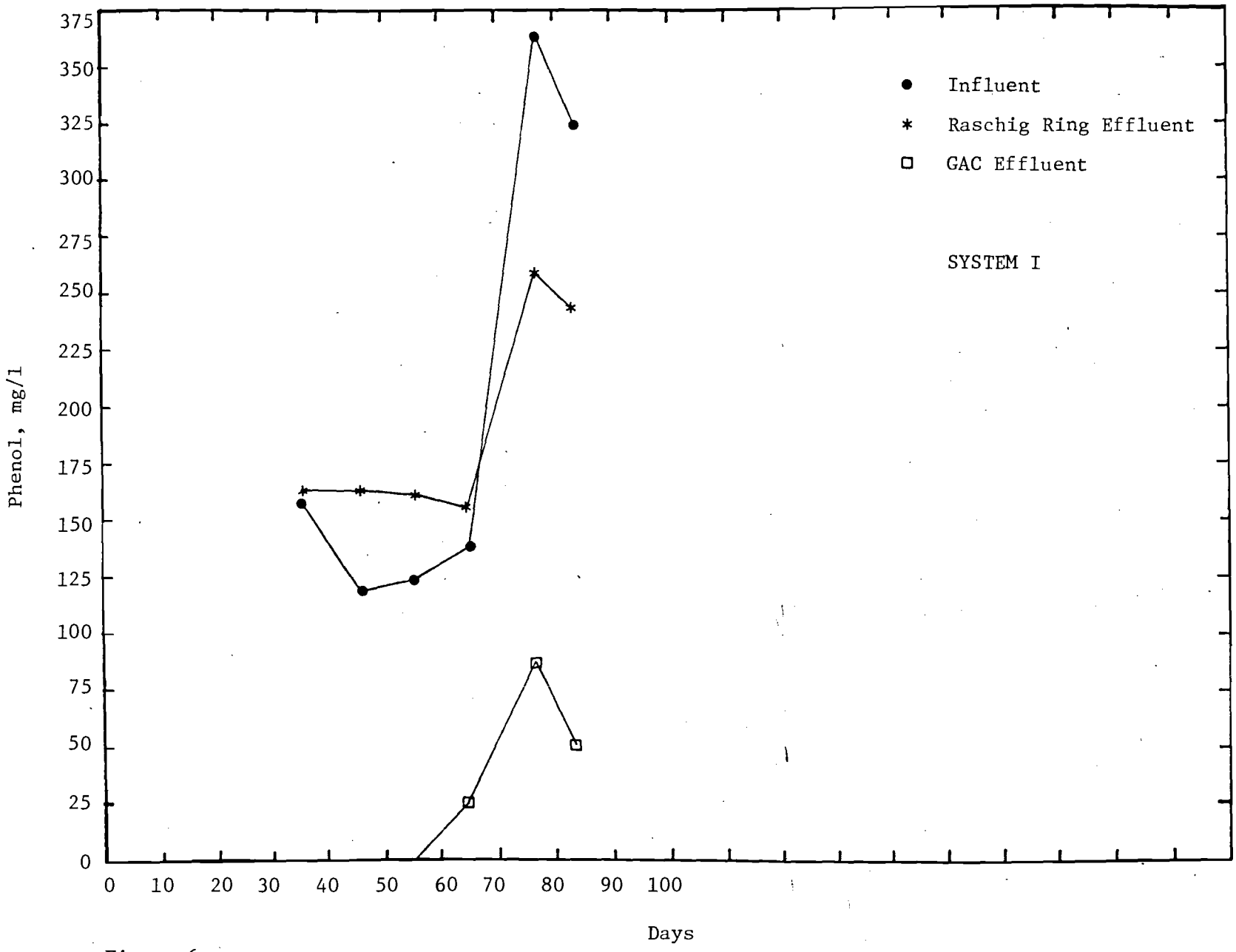

Phenol, mg/l
375
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100
Days
Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM I

Figure 6

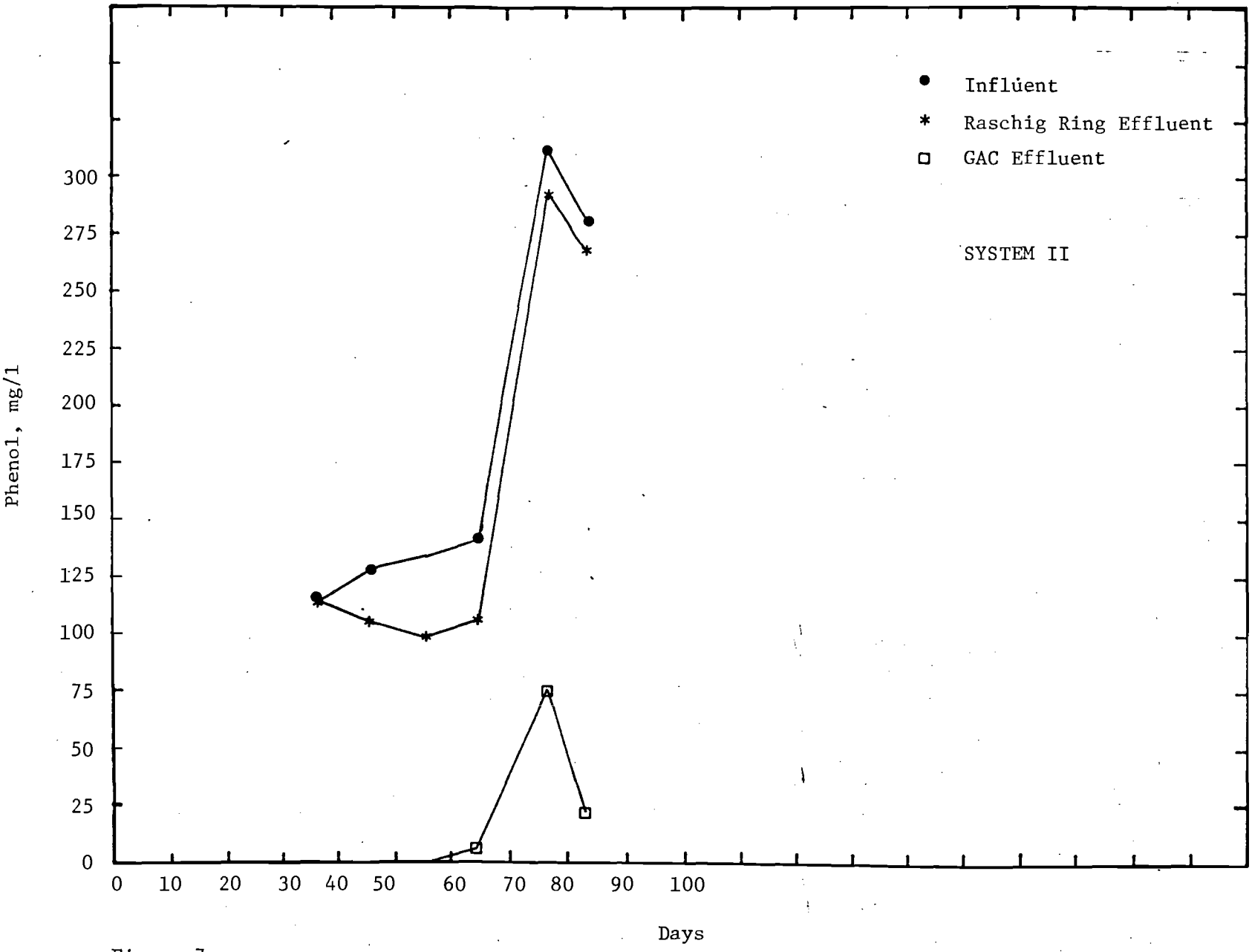

Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM II
Phenol, mg/l
300
275
250
225
200
175
150
125
100
75
50
25
0
0
10
20
30
40
50
60
70
80
90
100
Days

Figure 7

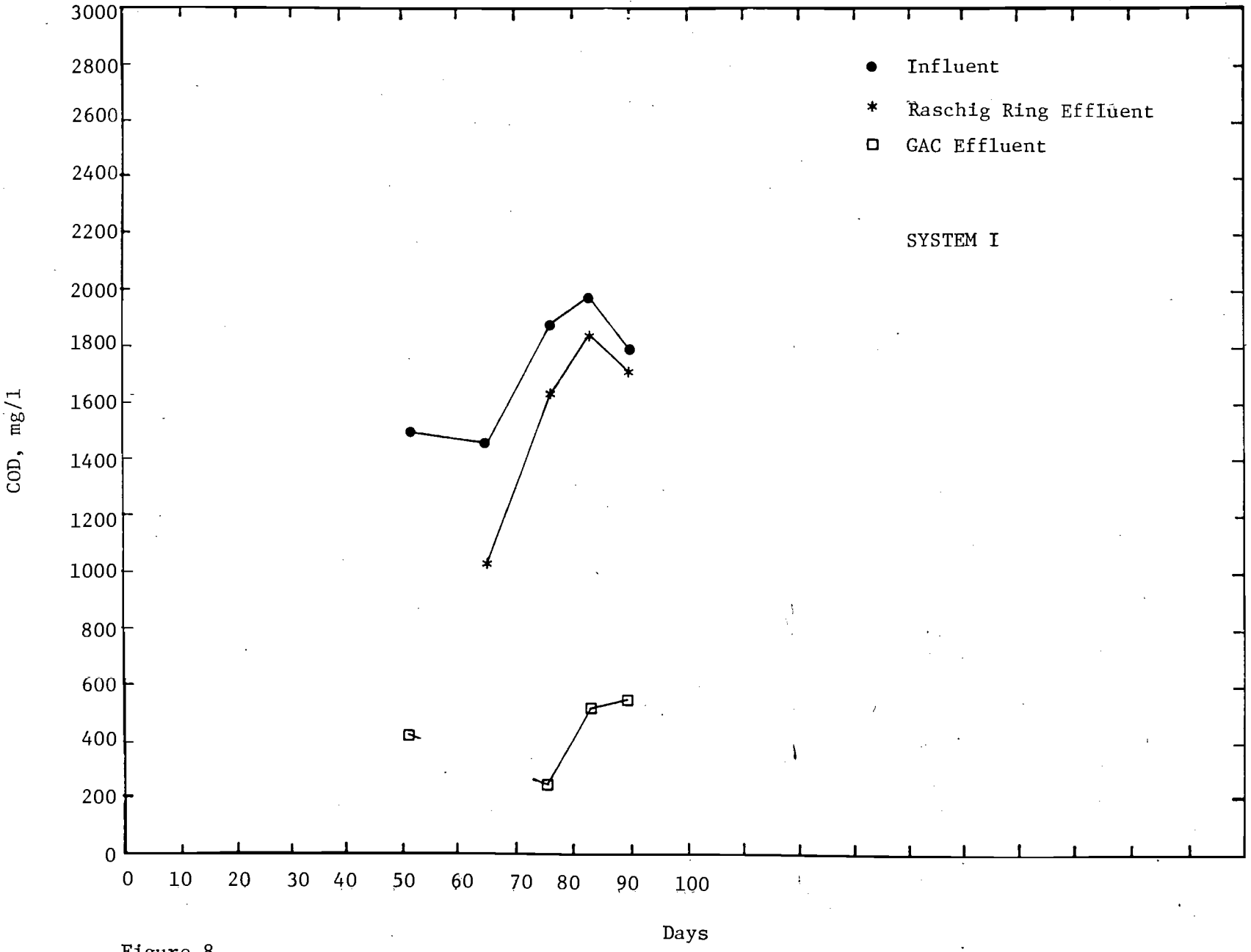

3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
COD, mg/l
0
10
20
30
40
50
60
70
80
90
100
Days
Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM I

Figure 8

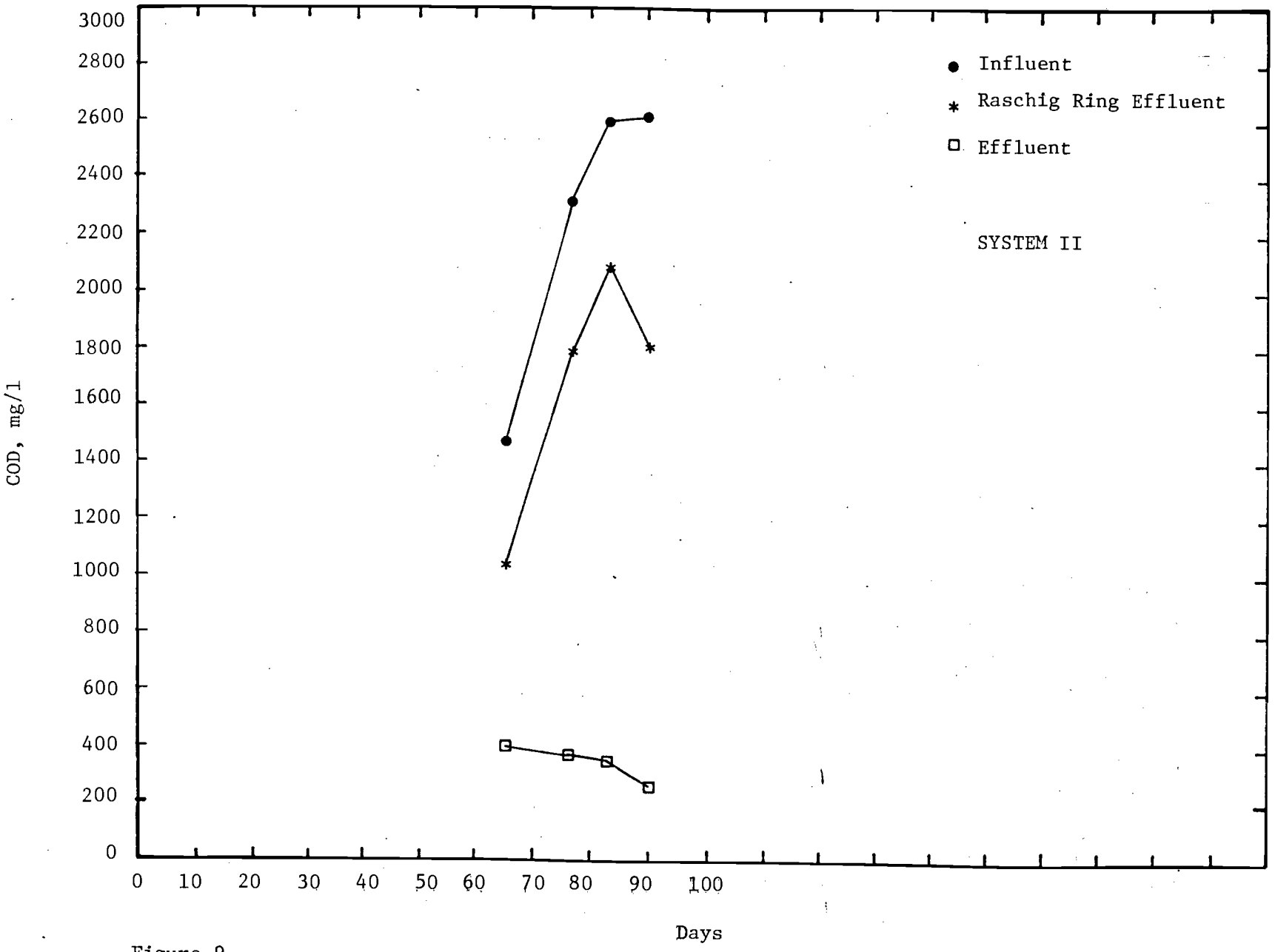

3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
COD, mg/l
0
10
20
30
40
50
60
70
80
90
100
Days
Influent
Raschig Ring Effluent
Effluent
SYSTEM II

Figure 9

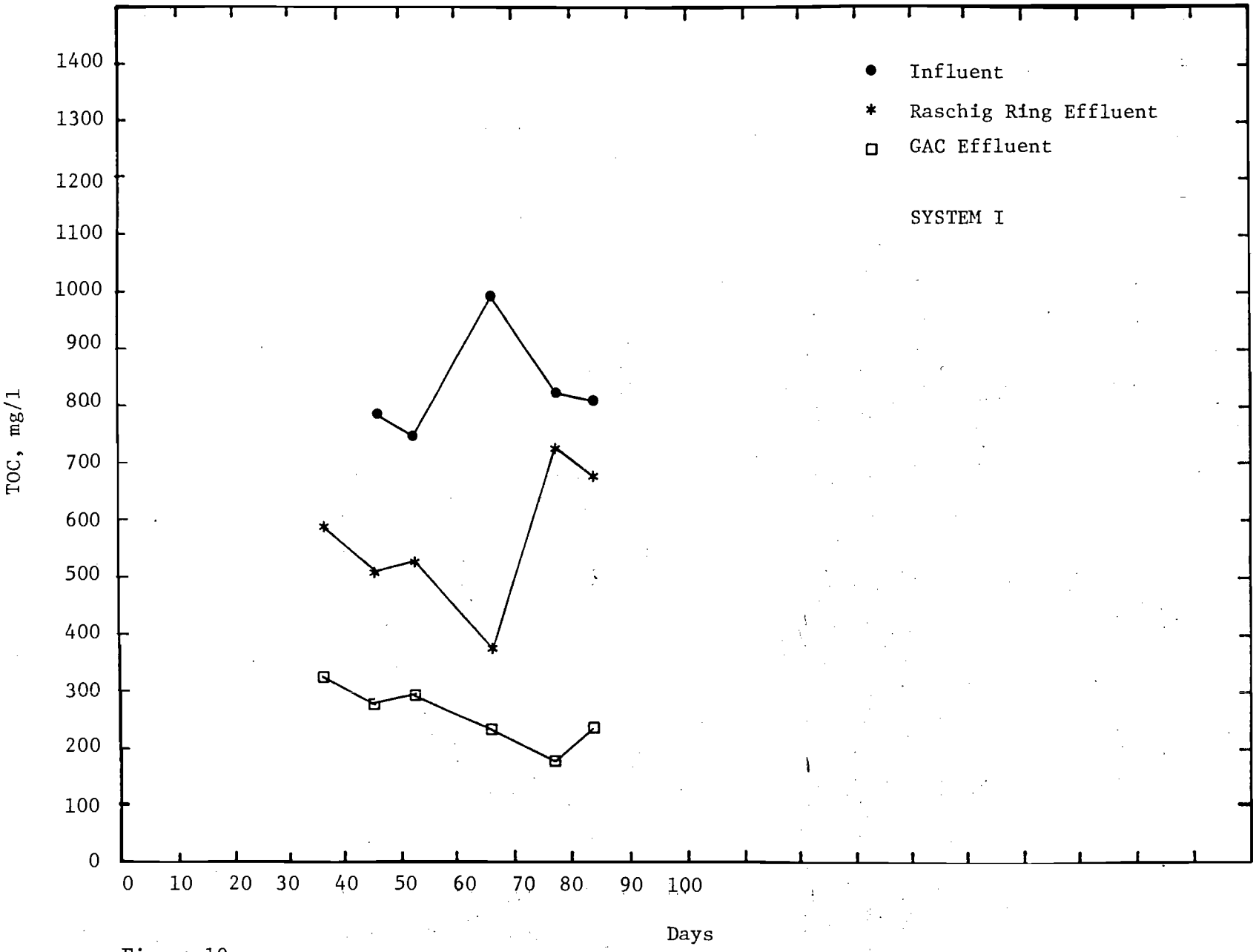

Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM I
TOC, mg/l
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 10 20 30 40 50 60 70 80 90 100
Days

Figure 10

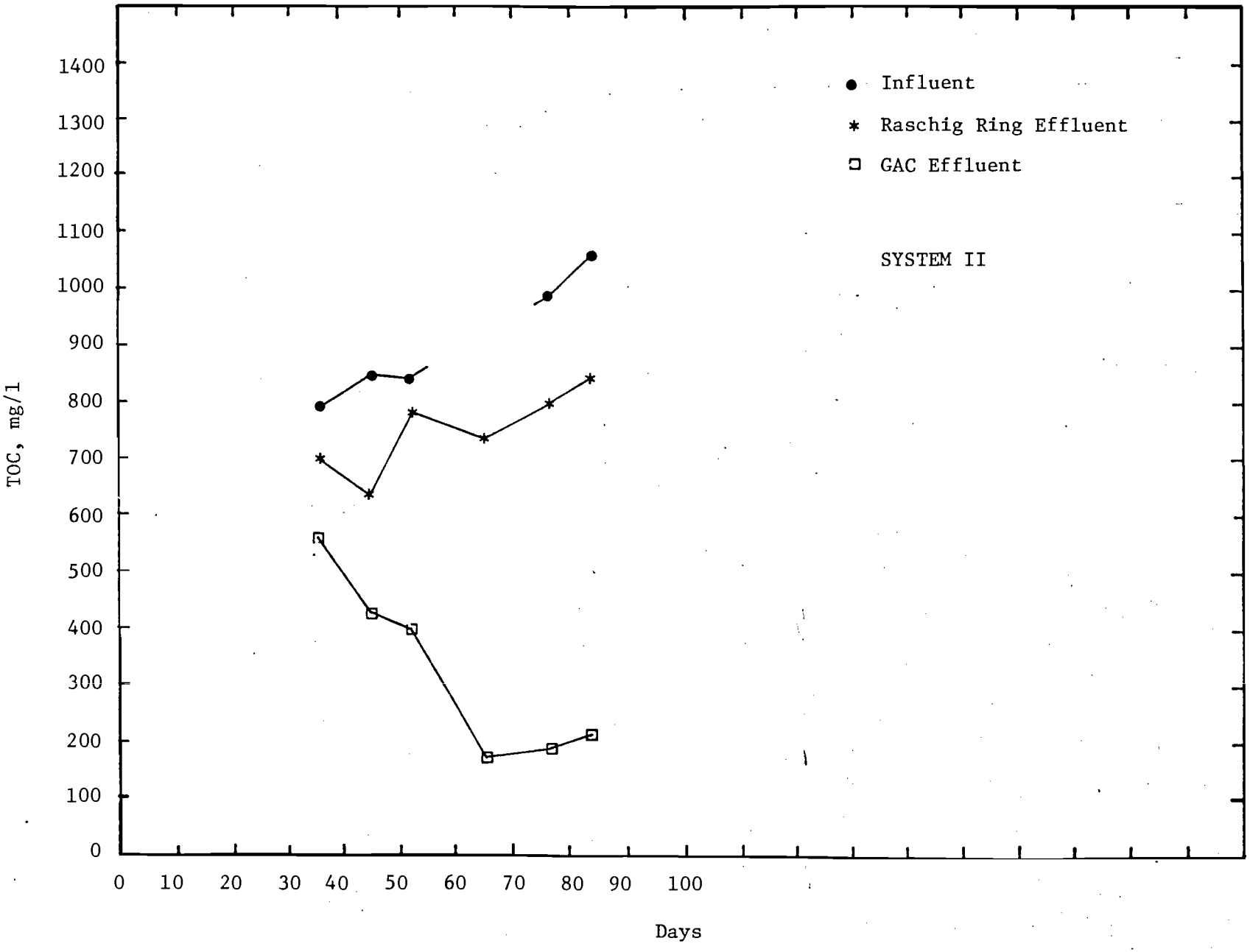

Influent
Raschig Ring Effluent
GAC Effluent
SYSTEM II
TOC, mg/l
Days
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
0
10
20
30
40
50
60
70
80
90
100

Figure 11

B. System III

1. Start Up

The third system was assembled and seeded in the same fashion as Systems I and II and began operation on December 22, 1981. Substrate containing wastewater (500 ppm TOC), glucose (500 ppm TOC) and phosphates is being used for acclimation of this system. Performance of this system will be monitored and the results will appear in succeeding reports.

III. GC/MS ANALYSIS

A. Introduction

A coal gasification wastewater sample from the Grand Forks Energy Technology Center was investigated for the identification of specific organic components. Two aliquots of the sample were solvent extracted by steam distillation vapour phase and stir-bar liquid-liquid techniques, fractionated by means of gel permeation chromatography (GPC) and submitted to HRGC-MS-DS analysis. The compounds identified and an estimate of their relative amounts are reported along with the general search computer report and reconstructed ion chromatograms.

B. Experimental Procedures

1 liter and 500 ml samples were subjected to steam distillation vapour phase and stir-bar liquid-liquid solvent extraction, respectively. Distilled in glass methylene chloride was used as solvent and the extraction was carried out in acidic (pH=2) and basic (pH=12) conditions. Concentration of the methylene chloride solution was achieved by Kuderna-Danish flask equipped with Snyder column. The GPC was carried out on Bio-Beads SX-2 (BioRAD Lab) gel that was slurry packed in a glass column 1 meter long and 1 cm internal diameter. A low pressure pump (Milton-Roy) was employed for solvent delivery and a micro sampling valve was used for sample injection. Pentane-methylene chloride (1:1) was used as solvent system. A Hewlett-Packard 5830A GC was interfaced with a Finnigan 4000 MS equipped with Nova 3 data system and Incos software package. The chromatography was carried out on a 30 m x 0.25 mm I.D. glass capillary column deactivated according to the persilylation method (Grob, 1980) and coated by the static method (Giabbai, 1978) with SE-54 gum phase. The sample transfer line between the GC and the ionization source consisted of approximately 40 cm long x 0.1 mm I.D. fused silica tubing. The experimental conditions were as follows:

GC
Splitless injection mode (30")
Temperature program 40°(3 min)-290°C at 4°C/min
Injector temperature 250°C

MS Electron Impact Ionization mode
Electron Energy 70 eV
Electron Multiplier 1500 V
Preamp Sensitivity 10^{-7} Amp/V
Emission Current 0.5 mAmp
Mass range 46-450 a.m.u.
Scan rate 1 scan/sec

The data were processed by a software program designated "Auto GC" developed at Finnigan Application Laboratory. The National Bureau of Standards mass spectra library, capable of approximately 25,000 mass spectra, was the reference basis for the tentative identification of the organic compounds.

C. Results

Figure 12 and 13 represent the reconstructed ion chromatogram of the samples extracted by steam distillation vapour phase under acidic and basic conditions, respectively. It is evident that the ionization source was overloaded by the presence of at least three major components. After further dilution of the extract it was possible to introduce an adequate amount for these three compounds and obtain proper ionization conditions. The three major peaks were identified as phenol, a cresol isomer and the third peak was the combination of the other two cresol isomers that were not resolved under the mentioned chromatographic conditions (Figure 14). Taking into consideration that 1) the compounds analyzed represent only the ones that are solvent extractable from water, 2) among the extractables only the ones directly amenable to GC were detected, 3) the MS response factors for all the compounds is considered the same, it is possible to roughly estimate that the sum of the amounts of phenol and cresols is at least 30 times higher than the sum of all the rest of the compounds detected. The amount of phenol itself is approximately 5 times higher than the amount of each cresol isomer. All the other components tentatively identified by the software program are reported in Figures 15 and 16.

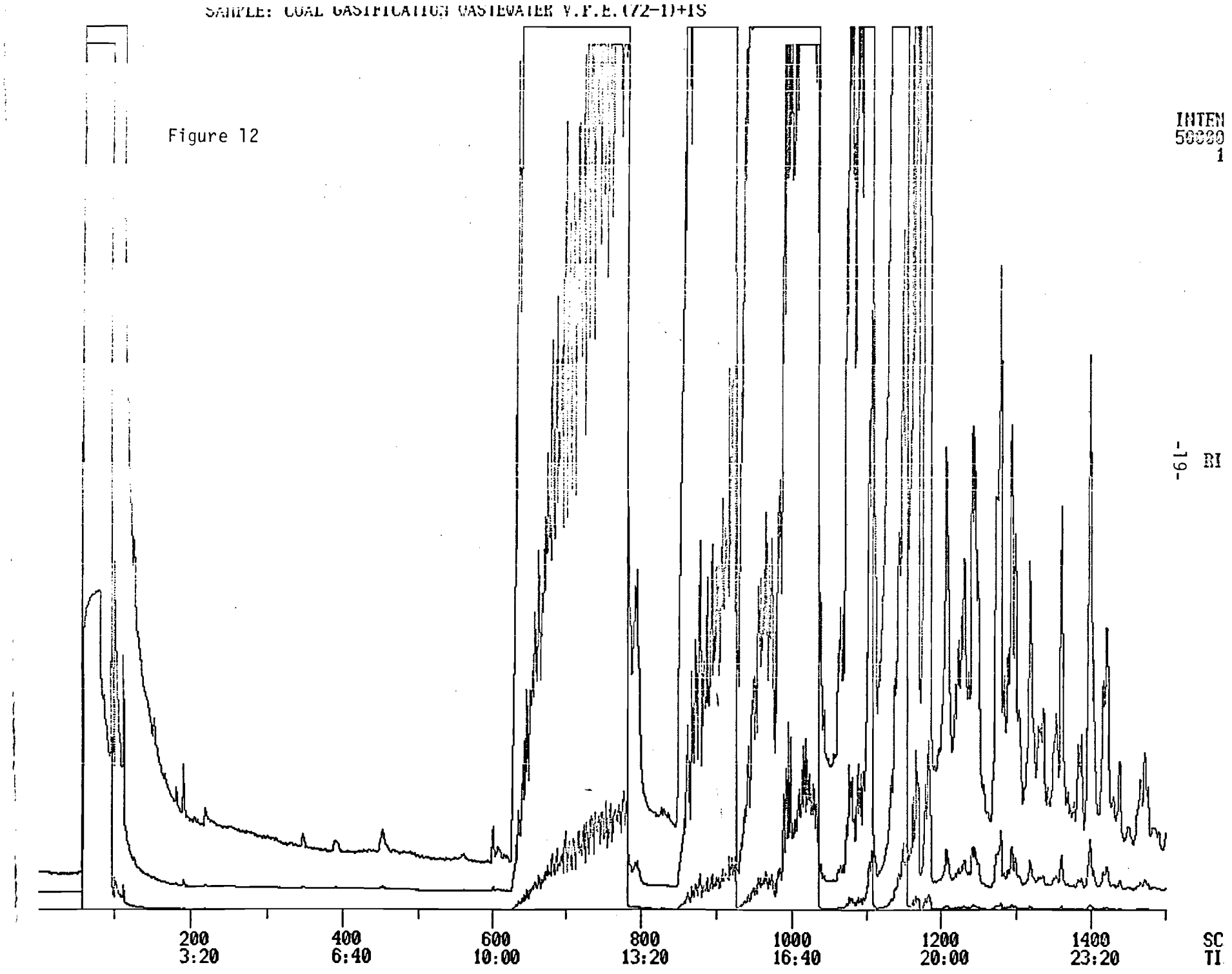

SAMPLE: COAL GASIFICATION WASTEWATER V.F.E.(72-1)+IS
Figure 12
INTEN
50000
1
200
3:20
400
6:40
600
10:00
800
13:20
1000
16:40
1200
20:00
1400
23:20
SC
TI

Figure 12 (continued)

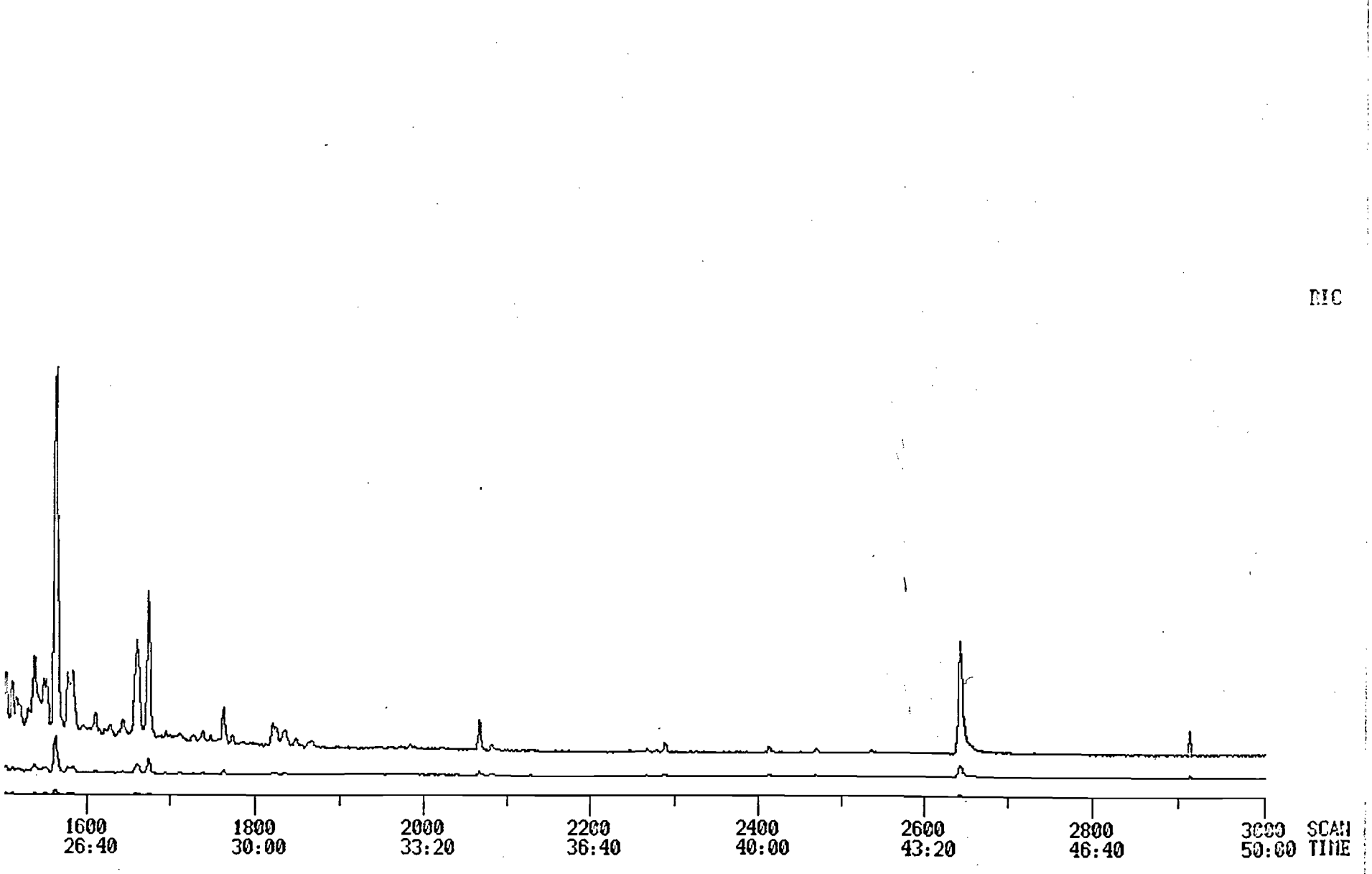


Figure 13

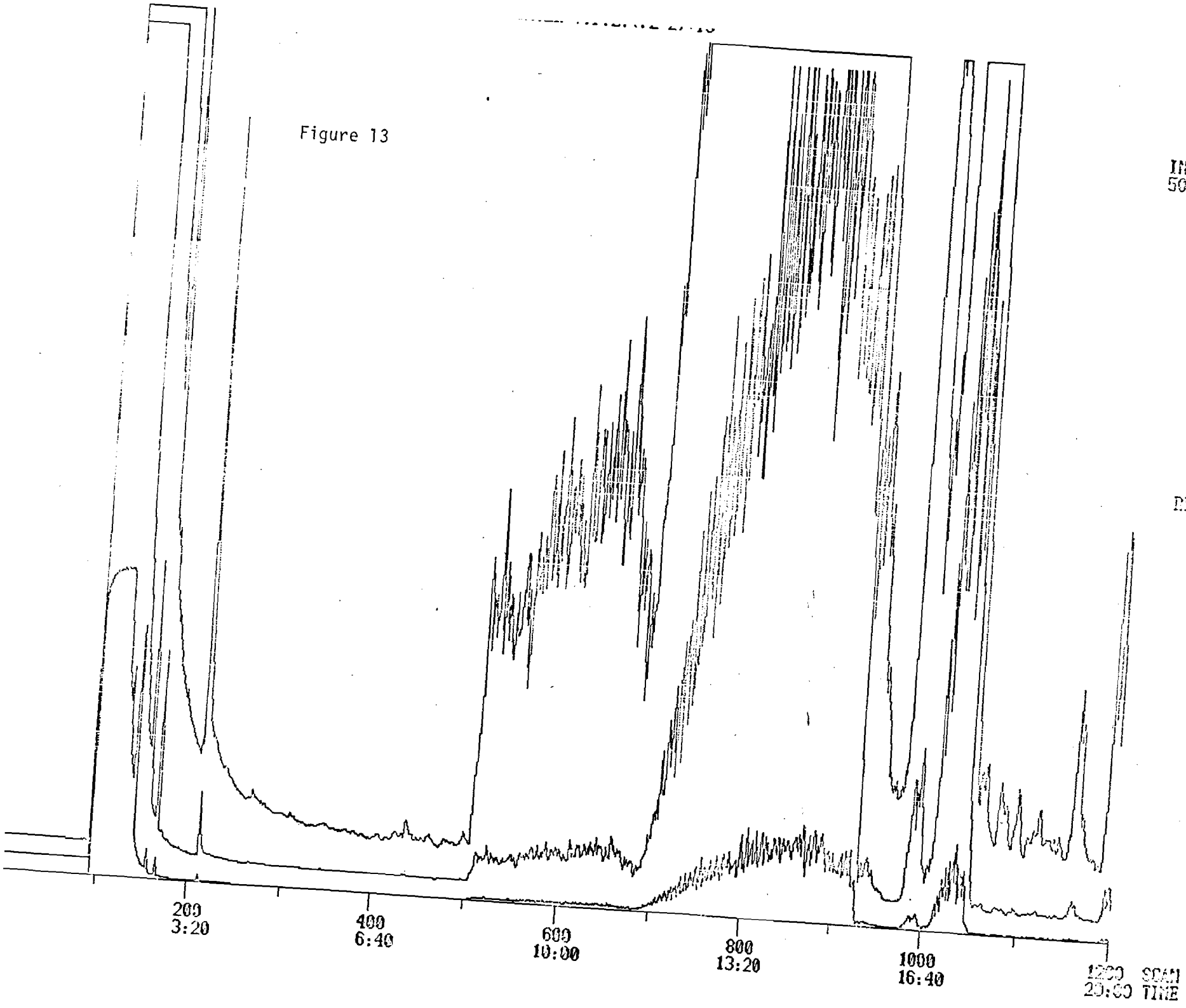

INTEN
50000.
1.
REC
200
3:20
400
6:40
600
10:00
800
13:20
1000
16:40
1200
20:00
SCAN
TIME

Figure 13 (continued)

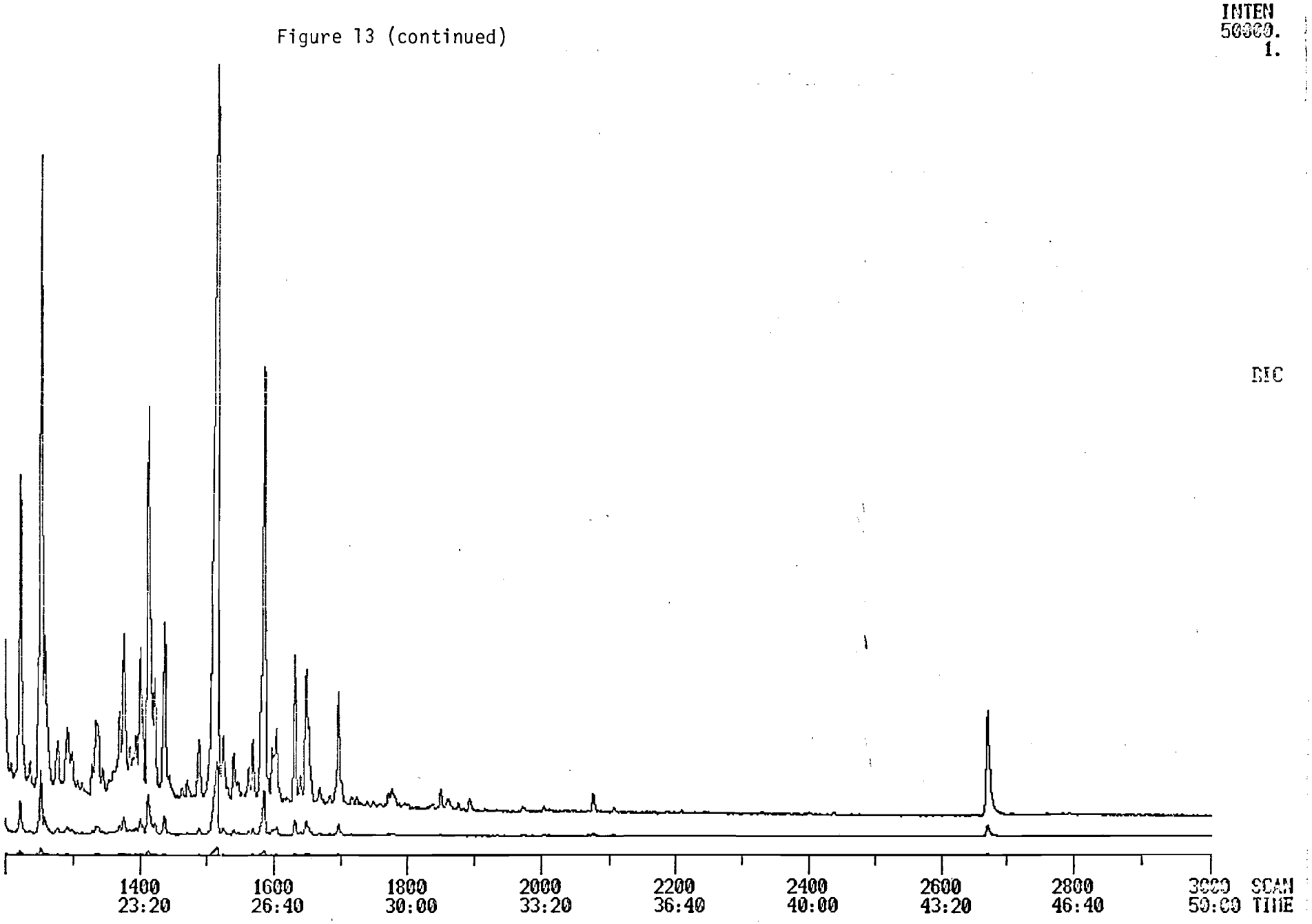
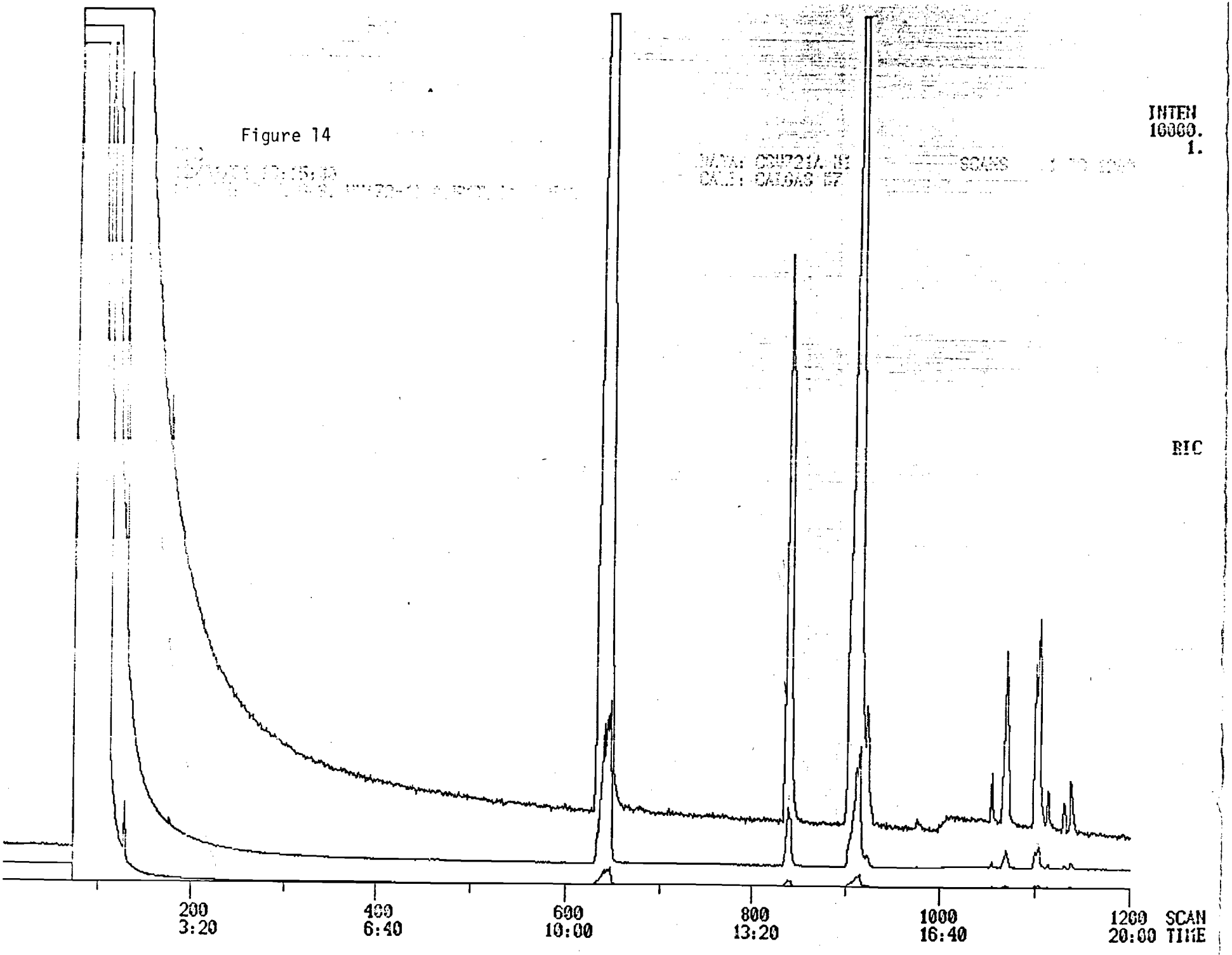


Figure 14


INTEN
10000.
1.
RIC
200
3:20
400
6:40
600
10:00
800
13:20
1000
16:40
1200
20:00
SCAN
TIME

CONDS.: SE54 30M,*84,40(3)300 4/M,SPLITLESS II
FORMULA: - INSTRUMENT: FINN I: 0
SUBMITTED BY: MFG ANALYST: MFG. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

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2	PHENOL,4-(1-METHYLETHYL)-	1231	956	820	NB	861	39128.	25.808	3.26
3	PHENOL,2-ETHYL-5-METHYL-	1243	960	871	NB	5449	122386.	80.725	10.19
4	UNKNOWN	1246	940	660	NB	6076			
5	5-ISOBENZOFURANCARBOXYLICACID,1,3-DIHYDRO-1,3-DIOXO-	1258	675	511	NB	2839	1599.	1.055	0.13
6	PHENOL,4-ETHYL-2-METHYL-	1281	938	802	NB	6076	151618.	100.000	12.62
7	PHENOL,2,3,5-TRIMETHYL-	1295	866	665	NB	3908	53783.	35.474	4.48
8	ETHANONE,1-(2,4-DIHYDROXYPHENYL)-	1300	908	747	NB	583	35886.	23.670	2.99
9	1H-INDOLE	1320	998	829	NB	1488	45739.	30.169	3.81
10	DECANE,3-BROMO-	1326	759	523	NB	16274	9907.	6.534	0.82
11	PROPANOICACID,2,2-DIMETHYL-,2-(1,1-DIMETHYLETHYL)PHENYLESTER	1331	666	368	NB	20924	4820.	3.179	0.40
12	NONANOICACID	1334	984	702	NB	1362	18618.	12.280	1.55
13	PHENOL,2,3,5-TRIMETHYL-	1337	987	784	NB	3908	14127.	9.318	1.18
14	BENZENEMETHANOL,AR-ETHENYL-	1343	795	660	NB	16282	1886.	1.244	0.16
15	1,3-BENZENEDIOL,4,5-DIMETHYL-	1351	881	568	NB	2678	7871.	5.192	0.66
16	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1355	953	506	NB	15415	11847.	7.814	0.99
17	BENZENEMETHANOL,AR-ETHENYL-	1362	969	761	NB	16282	42614.	28.108	3.55
18	2H-1-BENZOPYRAN-2-ONE,3,4-DIHYDRO-	1370	769	530	NB	1470	2298.	1.516	0.19
19	UNKNOWN	1374	698	467	ND	2974			
20	PHENOL,2-(1-METHYLPROPYL)-	1378	758	668	NB	575	2449.	1.616	0.20
21	2-PROPENAL,3-PHENYL-	1384	980	818	NB	1006	14596.	9.627	1.21
22	BENZOFURAN,7-METHYL-	1388	981	874	NB	11795	14629.	9.649	1.22
23	BENZENE,1-ETHYL-2,4,5-TRIMETHYL-	1400	880	706	NB	12129	95745.	63.152	7.97
24	UNKNOWN	1404	826	431	NB	6740			
25	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1417	989	824	NB	15415	34774.	22.936	2.89
26	UNKNOWN	1420	780	466	NB	17899			
27	2-PROPENAL,3-PHENYL-	1421	978	704	NB	1006	37618.	24.812	3.13
28	2-PROPENAL,3-PHENYL-	1422	981	754	NB	1006	37783.	24.921	3.14
29	BENZENEPROPANOL,2-HYDROXY-	1430	728	405	NB	5168	5003.	3.300	0.42
30	BENZENEMETHANOL,.ALPHA.-ETHYL-4-METHOXY-	1438	822	571	NB	8409	9519.	6.279	0.79
31	1,9-NONANEDIOL,DIMETHANESULFONATE	1451	726	397	NB	7695	2460.	1.622	0.20
32	DECANOICACID	1462	881	680	NB	2029	6580.	4.287	0.54
33	1-NAPHTHALENOL,1,2,3,4-TETRAHYDRO-	1466	769	519	NB	2692	11564.	7.627	0.96
34	1H-INDOLE,3-METHYL-	1467	974	598	NB	490	9363.	6.176	0.78
35	BENZENE,\2-(METHYLSULFINYL)ETHENYL\-	1472	721	436	NB	9726	13146.	8.671	1.09
36	2-PROPYN-1-OL,3-P-TOLYL-	1485	697	357	NB	11341	3298.	2.176	0.27
37	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1504	979	792	NB	15415	10401.	6.860	0.87
38	BENZENE,1,3-DIMETHYL-5-(1-METHYLETHYL)-	1512	887	423	NB	8007	4375.	2.886	0.36
39	BENZENE,2,4-DIMETHYL-1-(1-METHYLETHYL)-	1517	777	580	NB	8006	5094.	3.360	0.42
40	BENZENE,(1,1-DIMETHYLETHYL)METHYL-	1531	804	471	NB	15328	1807.	1.192	0.15
41	BENZENE,HEXAMETHYL-	1538	767	554	NB	549	14698.	9.695	1.22
42	1H-INDENE-1,2-DIOL,2,3-DIHYDRO-1-METHYL-,CIS-	1539	815	450	NB	24305	10990.	7.249	0.91
43	2-PROPYN-1-OL,3-P-TOLYL-	1549	834	663	NB	11341	5381.	3.549	0.45
44	BIPHENYLENE	1553	978	937	NB	1880	9014.	5.945	0.75
45	BENZENE,HEXAMETHYL-	1563	992	854	NB	549	66497.	43.861	5.53
46	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1577	959	771	NB	9337	9584.	6.322	0.80
47	2-PROPYN-1-OL,3-P-TOLYL-	1583	900	657	NB	11341	14062.	9.275	1.17
48	BENZENE,HEXAMETHYL-	1584	600	558	NB	549	9002.	5.938	0.75
49	ACENAPHTHYLENE,1,2-DIHYDRO-	1610	951	800	NB	488	3169.	2.090	0.26
50	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1628	890	572	NB	9337	2266.	1.494	0.19
51	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1644	833	635	NB	9337	2905.	1.916	0.24
52	2-NAPHTHALENOL	1662	992	690	NB	1678	17945.	11.836	1.49
53	2-NAPHTHALENOL	1675	988	834	NB	1678	21025.	13.868	1.75
54	1-NAPHTHALENOL,3-METHYL-	1739	928	802	NB	10488	1796.	1.185	0.15
55	1H-PHENALENE	1764	939	823	NB	1836	5589.	3.687	0.47
56	1-NAPHTHALENOL,3-METHYL-	1822	973	889	NB	10488	7255.	4.785	0.60
57	1-NAPHTHALENOL,3-METHYL-	1837	829	749	NB	10488	4479.	2.955	0.37
58	DIBENZOFURAN,4-METHYL-	1850	893	708	NB	9509	1063.	0.701	0.09
59	1H-PYRAZOLE,3-METHYL-5-PHENYL-	1868	732	614	NB	7024	2009.	1.325	0.17
60	PHENANTHRENE	2067	967	927	NB	518	5442.	3.589	0.45
61	PHOSPHINE,BIS(PENTAFLUOROPHENYL)PHENYL-	2289	845	785	NB	8245	1766.	1.165	0.15
62	BENZENETETRACARBOXYLLICACID TETRAMETHYLESTER	2643	822	744	NB	25414	31691.	20.903	2.64

SAMPLE: COAL GASIFICATION [illegible]
CONDS.: SE54 30M,*84,40(3)300 4/M,SPLITLESSINCL
FORMULA: PH12 [illegible] INSTRUMENT: FINN [illegible] WT.: 0.0000
SUBMITTED BY: MFG ANALYST: MFG. ACCT. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

NO	NAME	SCAN	FIT	PURITY	LIBRARY	ENTRY	AREA	AMOUNT	%TOT
1	ACETAMIDE,2,2,2-TRIFLUORO-N-METHYL-	1078	703	409	NB	4125	10232.	4.490	0.82
2	[H-1,2,3-TRIAZOLE-4-CARBOXYLICACID,4,5-DIHYDRO-1-PH [illegible]L-	1085	765	615	NB	21120	7747.	3.400	0.62
3	5(4H)-INDANONE,TETRAHYDRO-,TRANS-	1097	696	519	NB	7985	11346.	4.979	0.91
4	AZETIDINE,2-PHENYL-	1108	577	341	NB	13929	738.	0.324	0.06
5	1H-IMIDAZOLE,2-ETHYL-	1114	763	514	NB	4676	11086.	4.865	0.89
6	3-PENTEN-2-ONE,3-ETHYL-4-METHYL-	1121	920	737	NB	13789	9249.	4.059	0.75
7	PHENOL,2,4-DIMETHYL-	1131	873	734	NB	1045	5083.	2.231	0.41
8	CYCLOPENTANE,NITRO-	1137	880	530	NB	6465	1705.	0.748	0.14
9	4-PENTEN-1-OL	1141	731	360	NB	4151	3968.	1.741	0.32
10	BORNANAMINE,N,N,1-TRIMETHYL-1-PHENYL-	1153	733	660	NB	7186	2613.	1.147	0.21
11	PHENOL,3-ETHYL-	1159	983	903	NB	3417	61273.	26.891	4.94
12	UNKNOWN	1162	978	802	NB	3417			
13	CYCLOHEXENE,1-METHYL-4-(1-METHYLETHYL)-,(+)-	1180	751	564	NB	4952	2022.	0.888	0.16
14	PHENOL,2,5-DIMETHYL-	1194	980	888	NB	735	53967.	23.684	4.35
15	PHENOL,3,4-DIMETHYL-	1198	996	900	NB	726	59471.	26.100	4.79
16	CYCLOHEXANE,1,1'-(OXYDI-2,1-ETHANEDIYL)BIS\4-METHYL-	1209	794	345	NB	21604	1084.	0.476	0.09
17	BENZOFURAN,2,3-DIHYDRO-	1223	975	830	NB	2474	51433.	22.572	4.15
18	PHENOL,4-METHOXY-	1237	963	725	NB	1788	2906.	1.275	0.23
19	ISOQUINOLINE	1254	998	940	NB	1467	105388.	46.251	8.50
20	QUINOLINE	1259	983	915	NB	623	32501.	14.263	2.62
21	NICOTINONITRILE,1,4-DIHYDRO-1-METHYL-4-OXO-	1279	932	658	NB	4052	9239.	4.055	0.74
22	ISOQUINOLINE	1292	989	894	NB	1467	20674.	9.073	1.67
23	1,3-CYCLOHEXADIENE,1,2,6,6-TETRAMETHYL-	1299	755	408	NB	2614	2772.	1.216	0.22
24	BENZENE,(3-METHOXY-1-PROPENYL)-	1300	789	387	NB	11453	2415.	1.060	0.19
25	1H-INDEN-1-ONE,2,3-DIHYDRO-	1314	933	828	NB	489	1643.	0.721	0.13
26	2-PROPENENITRILE	1328	975	545	NB	1111	5888.	2.584	0.47
27	UNKNOWN	1335	992	744	NB	1488			
28	1H-INDOLE	1338	984	932	NB	1488	18627.	8.175	1.50
29	1,3-BENZENEDIOL,4-ETHYL-	1344	816	368	NB	6734	2400.	1.053	0.19
30	1,3-BENZENEDIOL,4,5-DIMETHYL-	1353	820	704	NB	2678	2375.	1.042	0.19
31	ISOQUINOLINE,3-METHYL-	1370	946	848	NB	4820	19221.	8.435	1.55
32	BENZENEMETHANOL,AR-ETHENYL-	1376	970	744	NB	16282	29177.	12.805	2.35
33	2,5-CYCLOHEXADIENE-1,4-DIONE,2,3,5,6-TETRAMETHYL-	1384	892	852	NB	2675	6041.	2.651	0.49
34	UNKNOWN	1386	842	550	NB	2675			
35	BENZENEETHANOL,3-HYDROXY-	1391	759	588	NB	10375	7357.	3.229	0.59
36	FORMAMIDE,N-PHENYL-	1394	874	788	NB	977	8970.	3.937	0.72
37	2-PROPENAL,3-PHENYL-	1401	983	792	NB	1006	29286.	12.853	2.36
38	BENZENEMETHANOL,AR-ETHENYL-	1413	959	808	NB	16282	82798.	36.338	6.67
39	BENZOFURAN,7-METHYL-	1422	947	540	NB	11795	11420.	5.012	0.92
40	BENZOFURAN,7-METHYL-	1437	977	697	NB	11795	24237.	10.637	1.95
41	QUINOLINE,3-METHYL-	1444	930	831	NB	3331	2664.	1.169	0.21
42	QUINOLINE,5-METHYL-	1463	879	553	NB	9695	1090.	0.478	0.09
43	QUINOLINE,4-METHYL-	1471	968	865	NB	2446	3036.	1.333	0.24
44	BENZENECARBOXIMIDOYLBROMIDE,N-METHYL-	1489	876	616	NB	19082	8458.	3.712	0.68
45	ETHANONE,1-PHENYL-,OXIME	1516	872	668	NB	3346	227859.	100.000	18.37
46	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1525	933	807	NB	15415	9664.	4.241	0.78
47	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1540	992	822	NB	15415	7197.	3.159	0.58
48	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1547	925	776	NB	15415	2366.	1.038	0.19
49	2-PROPYN-1-OL,3-P-TOLYL-	1563	917	746	NB	11341	5083.	2.231	0.41
50	NAPHTHALENE,1,2,3,4-TETRAHYDRO-1-METHYL-	1569	830	694	NB	5249	8601.	3.810	0.70
51	BENZENE,HEXAMETHYL-	1585	992	881	NB	549	89901.	39.455	7.25
52	1H-PYRROLO\2,3-B\PYRIDINE	1597	912	542	NB	1889	6863.	3.012	0.55
53	2-PROPYN-1-OL,3-P-TOLYL-	1604	927	717	NB	11341	16915.	7.423	1.36
54	AZETIDINE,2-PHENYL-	1632	835	703	NB	13929	22633.	9.933	1.82
55	ETHANOL,2-(1-PHENYLHYDRAZINO)-	1639	816	617	NB	19496	4489.	1.970	0.36
56	BENZENEETHANAMINE,N-(PHENYLMETHYLENE)-	1648	713	564	NB	6950	33343.	14.633	2.69
57	2-PENTEN-1-ONE,1-(2-HYDROXY-5-METHYLPHENYL)-	1667	668	411	NB	19996	2121.	0.931	0.17
58	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1683	891	735	NB	9337	1135.	0.498	0.09
59	2-NAPHTHALENOL	1696	908	889	NB	1678	19380.	8.505	1.56
60	BENZO\B\THIOPHENE,2,7-DIMETHYL-	1716	732	489	NB	11555	859.	0.377	0.07
61	BENZENEETHANAMINE,N-(PHENYLMETHYLENE)-	1723	777	466	NB	6950	894.	0.393	0.07
62	1H-BENZIMIDAZOLE-2-CARBOXALDEHYDE	1772	630	482	NB	7000	2061.	0.904	0.17
63	ETHANONE,1-PHENYL-,OXIME	1777	829	513	NB	3346	3041.	1.334	0.25
64	1-NAPHTHALENOL,3-METHYL-	1851	959	833	NB	10488	3495.	1.534	0.28
65	1-NAPHTHALENOL,3-METHYL-	1861	810	704	NB	10488	2653.	1.164	0.21
66	1,4-NAPHTHALENEDIONE,2,3-DIMETHYL-	1877	933	801	NB	6035	1059.	0.465	0.09
67	1-NAPHTHALENOL,3-METHYL-	1893	890	707	NB	10438	2677.	1.175	0.22
68	ISOQUINOLINE,1-ETHYL-	2077	749	402	NB	9699	2909.	1.277	0.23
69	BENZENETETRACARBOXYLLICACID TETRAMETHYLESTER	2671	824	746	NB	25414	29708.	13.038	2.39

IV. SOLVENT EXTRACTION

A. Experimental Procedure

Organic free water was spiked with concentrations of phenol ranging from 0.1 to 1,000 mg/l. 200 ml aliquots of the spiked phenol were then extracted with 50 ml of methyl isobutyl ketone. The two phases were separated the organic phase was reduced in volume and analyzed for phenol by capillary column gas chromatography. The aqueous phasewas acidified to pH 2 and extracted with three 25 ml portions of methylene chloride. The methylene chloride was dried and concentrated to a small volume and analyzed for phenol using capillary column gas chromatography

The results from the above analysis were used to calculate the distribution coefficient for phenol.

To obtain data which would be more representative of actual wastewater extraction the above procedure was repeated using solvent extracted (MIBK) wastewater in the place of the organic free water. The solvent extracted wastewater was prepared by extracting raw wastewater with 5 portions of MIBK.

B. Results

Distribution coefficients obtained from using spiked organic free water had values ranging from 88 to 95 with an average of 91. These values agree well with those reported in the literature. However, the results using extracted wastewater as the diluent were inconclusive. The methylene chloride back extraction of the acidified wastewater tended to concentrate the acid species which were not extracted by the MIBK. These species severly interfered with the gas chromatographic analysis for phenol and reliable data could not be obtained.

Extraction recovery data for known samples was quite good with phenol recoveries averaging 113% with an average aeriation of 21%.

C. Extractor Design

Using the preliminary data from the organic free water extractions the design for the staged continuous laboratory extractor is given in Figure 17 and the overall extraction process unit is illustrated in Figure 18. The extractor will be constructed of three inch galvanized pipe and fitting. Each section will be 6 inches long giving a volume of approximately 700 ml per section. A five stage unit would therefore have an overall volume of 3.5 liters.

Operation of the unit would involve charging the unit with wastewater and solvent and then: 1) opening valves A and C and allowing approximately 550 ml of wastewater to flow through the system and close value A and C; 2) allow the mixed system to phase separate; 3) open valves B and D) and allow approximately 150 ml of solvent to flow through the system and then close valves B and D; 4) allow the mixed system to phase separate; and 5) repeat steps 1 through 4 until the desired volume of wastewater has been treated.

V. FUTURE WORK

Acclimation of Systems I, II and III will continue until one system is at psuedo-steady state. At that time the acclimated system will be used for the initial loading studies as outlined in the project proposal while the other two systems continue to acclimate. Additional efforts will be made to assure that all systems are receiving raw wastewater of identical composition.

Construction of the solvent extractor will begin and efforts will be made to obtain K_d values using raw wastewater as the diluent by first extracting the raw wastewater with methylene chloride at pH 2 to remove those species interfering with the phenol analysis. The CH_2CL_2 extracted raw wastewater will then be neutralized to pH 7 to 8 and used as the diluent.

Literature surveys pertaining to the nitrification system will be completed.

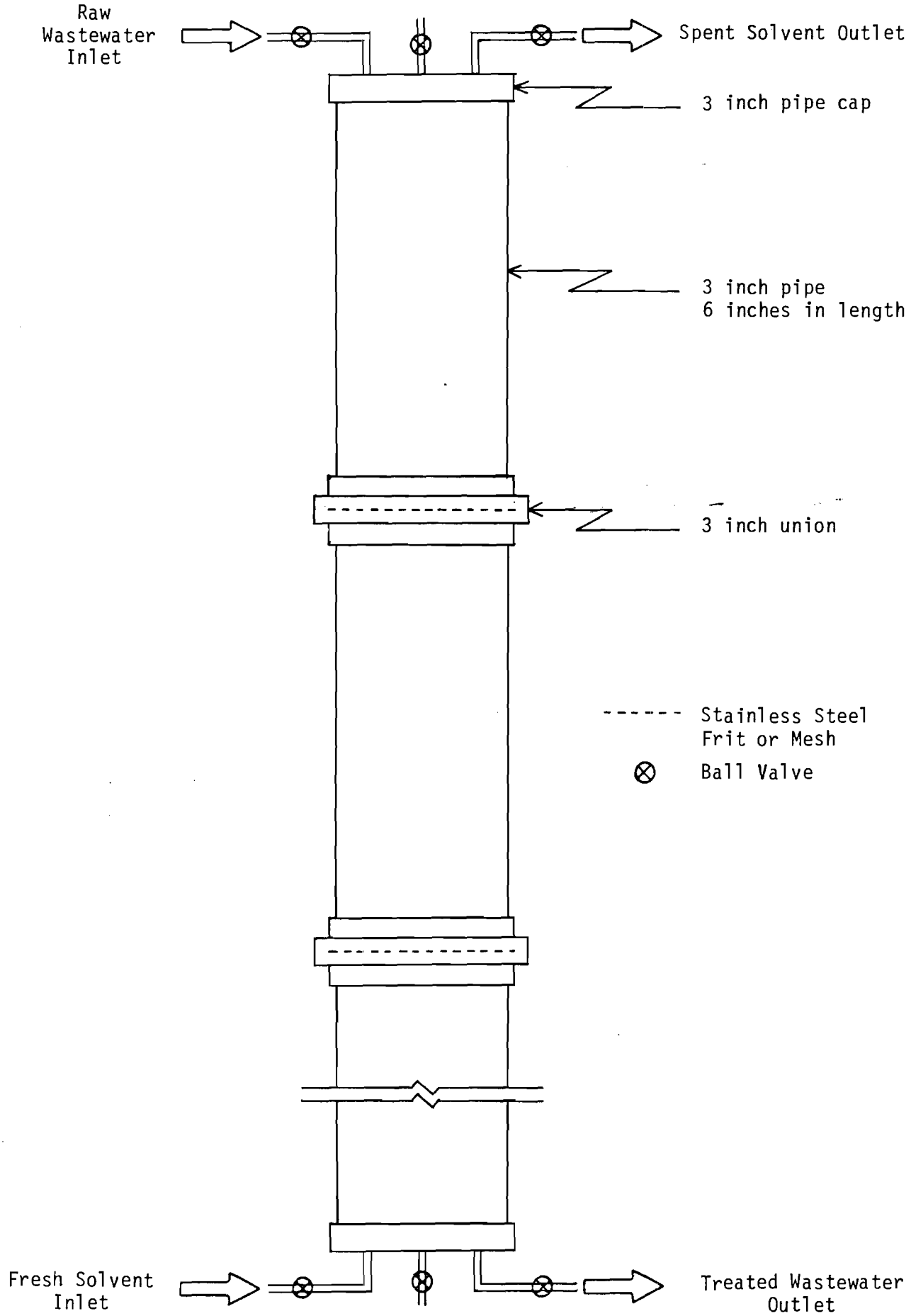
Raw
Wastewater
Inlet
Spent Solvent Outlet
3 inch pipe cap
3 inch pipe
6 inches in length
3 inch union
Stainless Steel
Frit or Mesh
Ball Valve
Fresh Solvent
Inlet
Treated Wastewater
Outlet

Figure 17

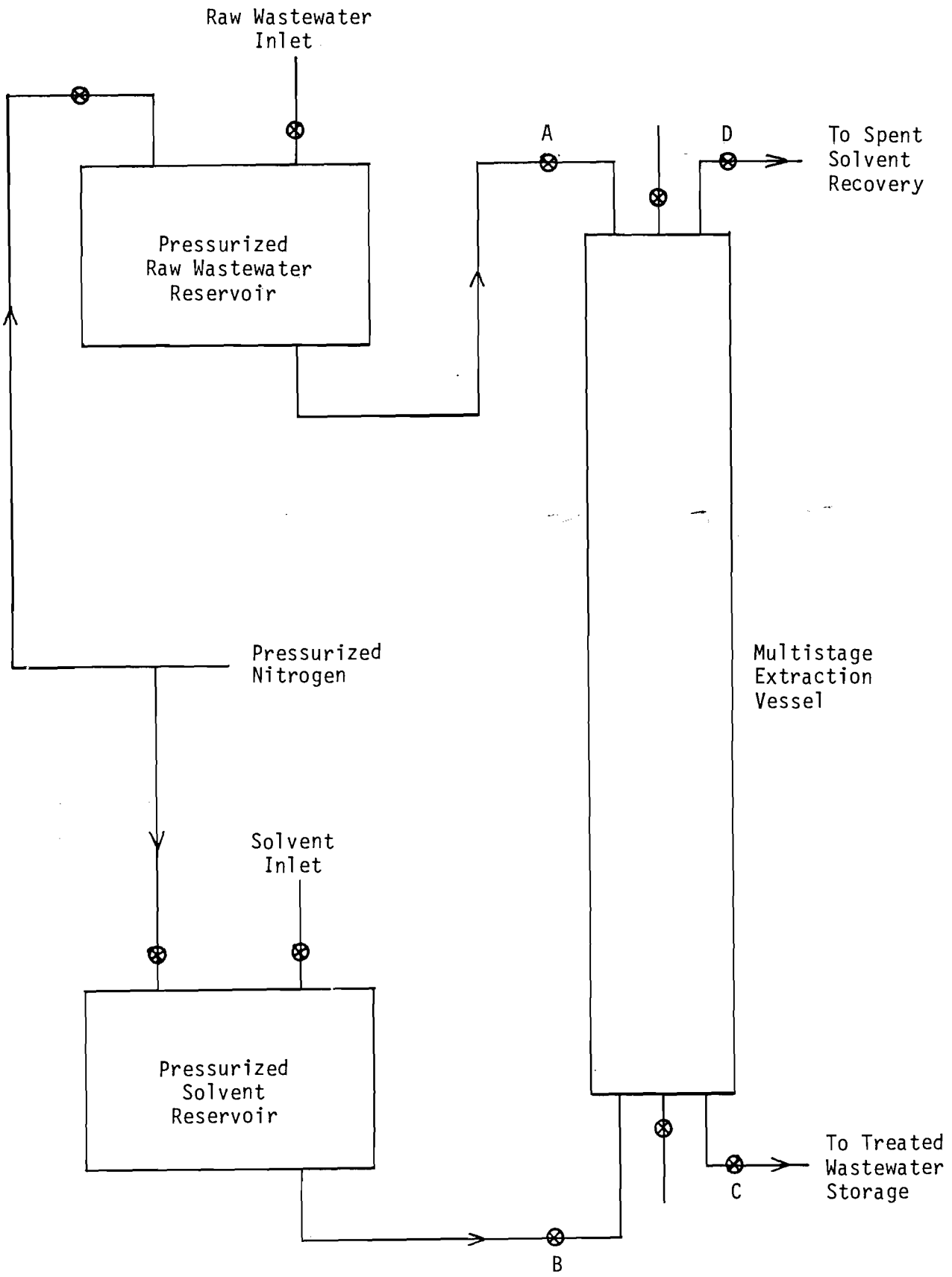
Raw Wastewater Inlet
Pressurized Raw Wastewater Reservoir
A
D
To Spent Solvent Recovery
Pressurized Nitrogen
Multistage Extraction Vessel
Solvent Inlet
Pressurized Solvent Reservoir
To Treated Wastewater Storage
C
B

Figure 18

The nitrification systems will be assembled and initial operation of these systems will begin.

Analysis for inorganic species will be incorporated into the process monitoring and development of ion chromatographic procedures will begin.

GC/MS work will focus on better estimates of the concentration level of phenol, cresols and other major identified components by updating the response factors of the MS with standard solutions of the aforementioned compounds. Further, the confirmation of the identity of other major and minor components will be pursued by chemical ionization techniques, pure compounds analysis under the same experimental conditions and eventually by fractionating the extracts by a preliminary separation by high performance liquid chromatography.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #3
April 1982

by

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TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from January 1, 1982 through March 31, 1982 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward the continued acclimation of three anaerobic treatment systems, construction and start up of an activated sludge nitrification system, construction and start up of a solvent extraction system and construction of an air stripping tower for ammonia removal. The progress of these efforts are depicted in the Gannt Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.

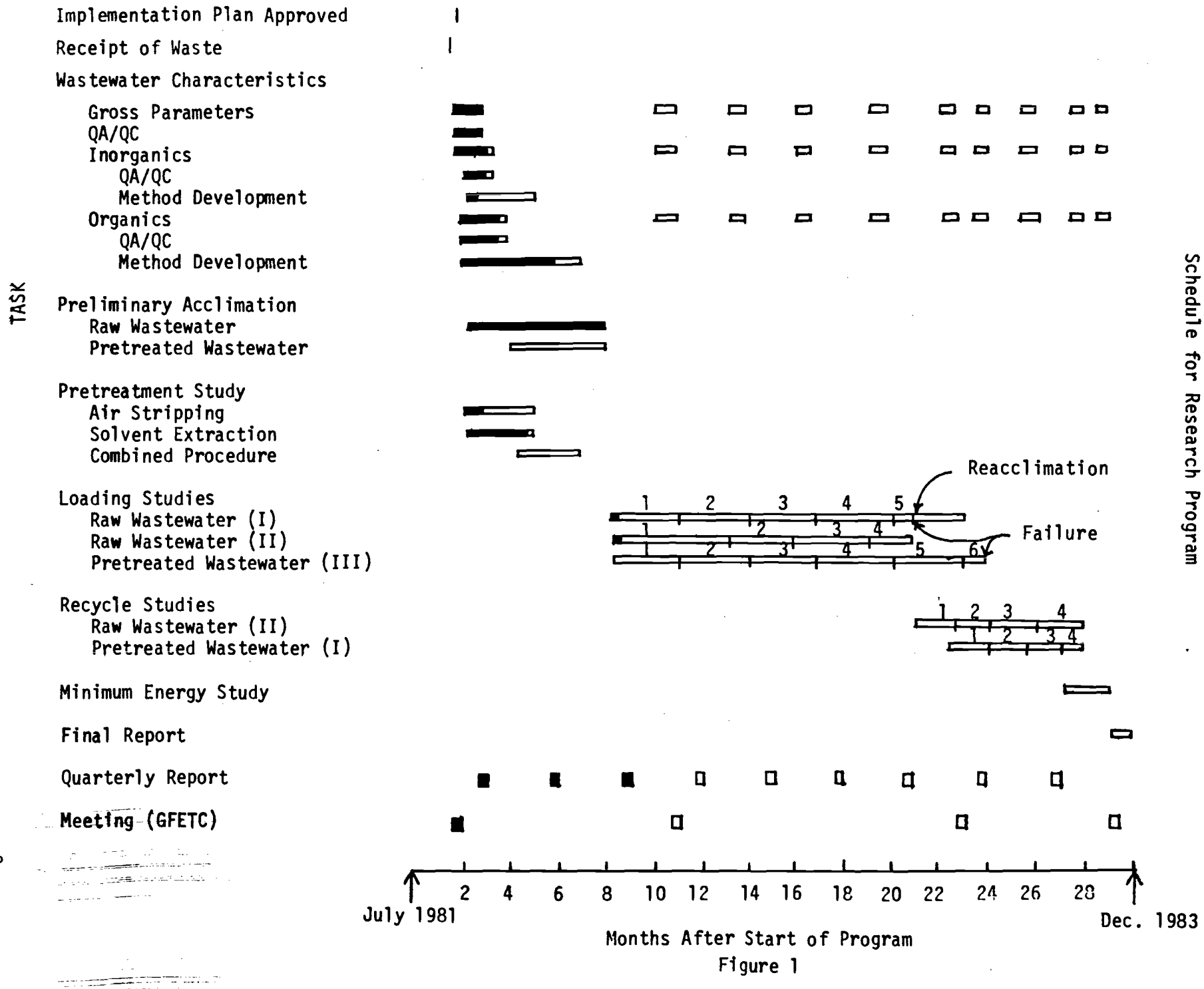
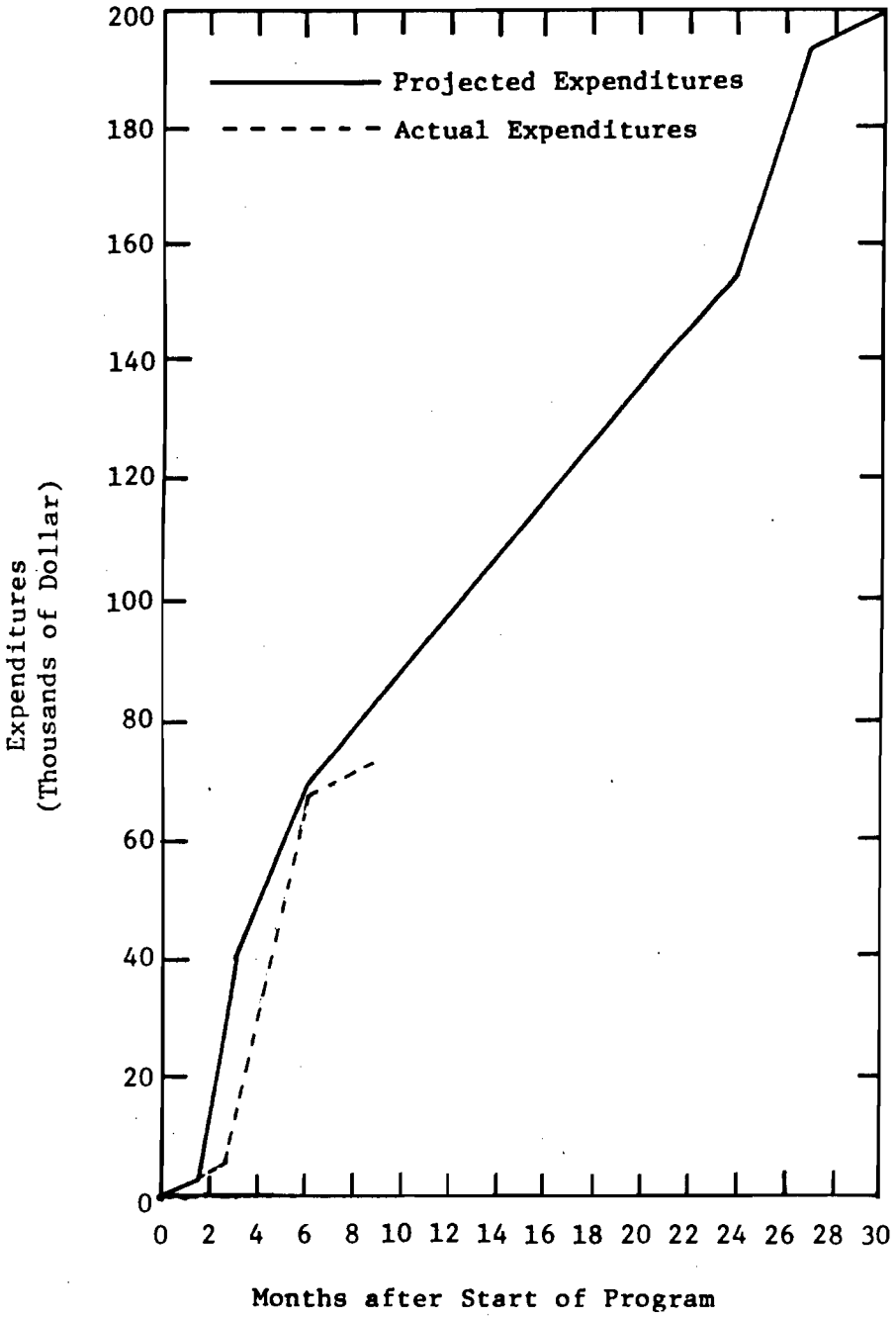

TASK
Implementation Plan Approved
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
Method Development
Preliminary Acclimation
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
July 1981
Dec. 1983
Months After Start of Program
Schedule for Research Program

Figure 1



Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

Figure 2.

II. ANAEROBIC TREATMENT SYSTEMS

A. Systems I and II

1. Operation and Acclimation

Systems I and II have been operated since the last quarterly report for an additional period of 90 days (day 84-174). During this time System I received diluted wastewater, phosphates and anaerobic phenol effluent for a 63 day period (Table 1) while System II was receiving diluted wastewater, phosphates, anaerobic phenol effluent and periodically reduced amounts of glucose (Table 1). On day 147 of continuous operation both systems began receiving identical feed substrates of diluted wastewater and phosphates. The influent flow rate was increased to 10 ml/min and the anaerobic phenol effluent supplement to the granular activated carbon columns was discontinued. Systems I and II have now been in operation for a period of 27 days (day 147-174) under identical loading conditions.

2. Volatile Acid Production

Concentrations of volatile acids in the effluents of both systems have shown a fairly regular decrease to relatively low levels (Figure 3 and 4) indicative of continued acclimation of the treatment system and greater conversion of the volatile acids to methane and carbon dioxide. Variation in volatile acid concentrations in the effluent are due primarily to changes in the feed to the systems causing minor upsets in the system performance.

The lower levels of volatile acids in the final effluent are indicative of the establishment of a viable population of methane forming bacteria in the treatment system.

3. Gas Production

Both System I & II are producing large quantities of CH_4 and CO_2 (Figures 5 & 6). Average quantities for the last 27 days (day 147 to 174) have been

TABLE 1. Feed Solution For System I and II

Days of Operation	Feed Solution
84-112	System I - Raw Wastewater (1260 ppm TOC), Phosphates, Anaerobic Phenol Effluent System II - Raw Wastewater (700 ppm), Glucose (300 ppm), Phosphates, Anaerobic Phenol Effluent
112-147	System I - Raw Wastewater (1000 ppm TOC), Phosphates, Anaerobic Phenol Effluent System II - Raw Wastewater (790 ppm TOC), Glucose (200 ppm TOC), Phosphates, Anaerobic Phenol Effluent
147-174	System I & II - Raw Wastewater (1042 ppm TOC), Phosphates

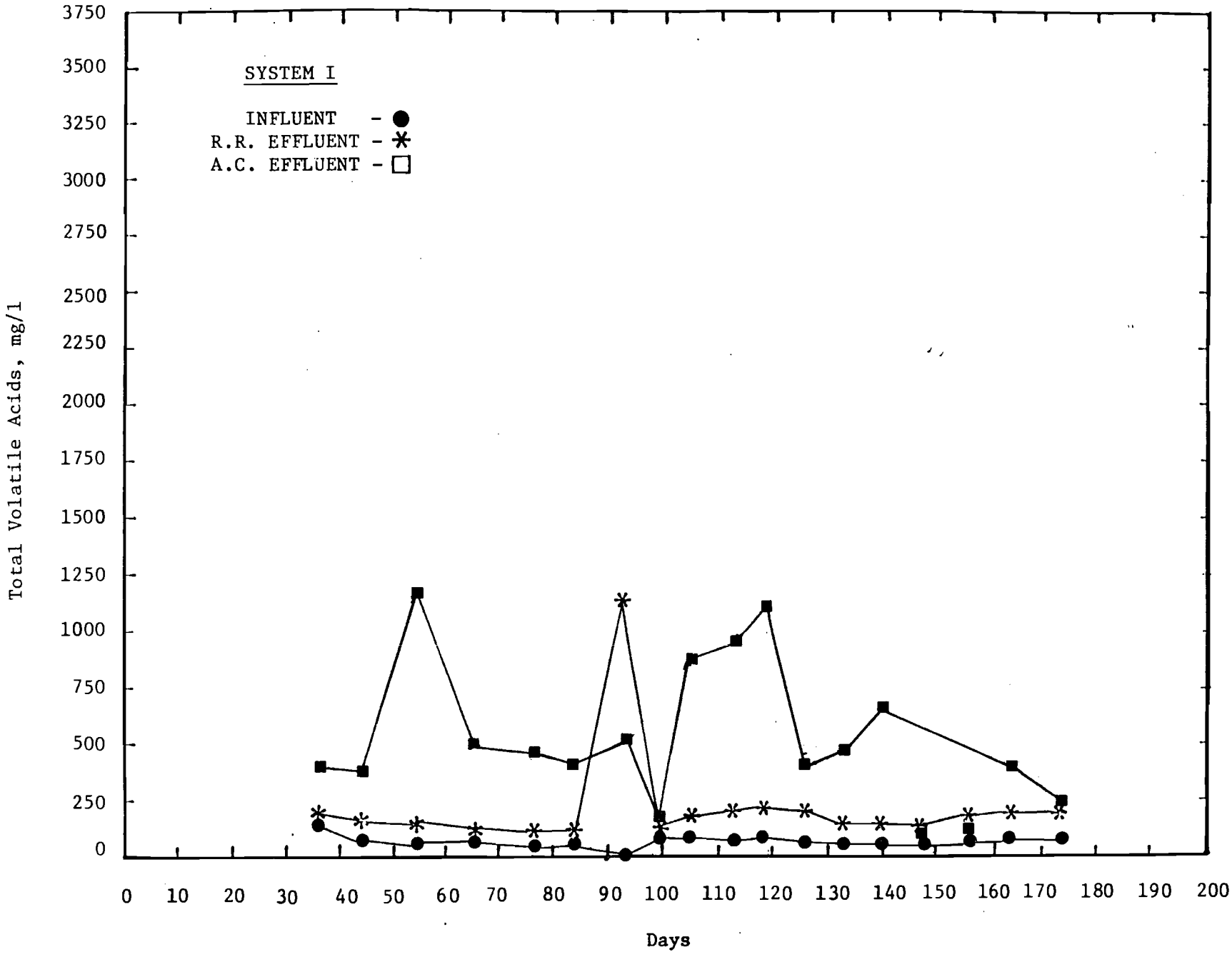

SYSTEM I
INFLUENT - ●
R.R. EFFLUENT - ✱
A.C. EFFLUENT - □
Total Volatile Acids, mg/l
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 3.

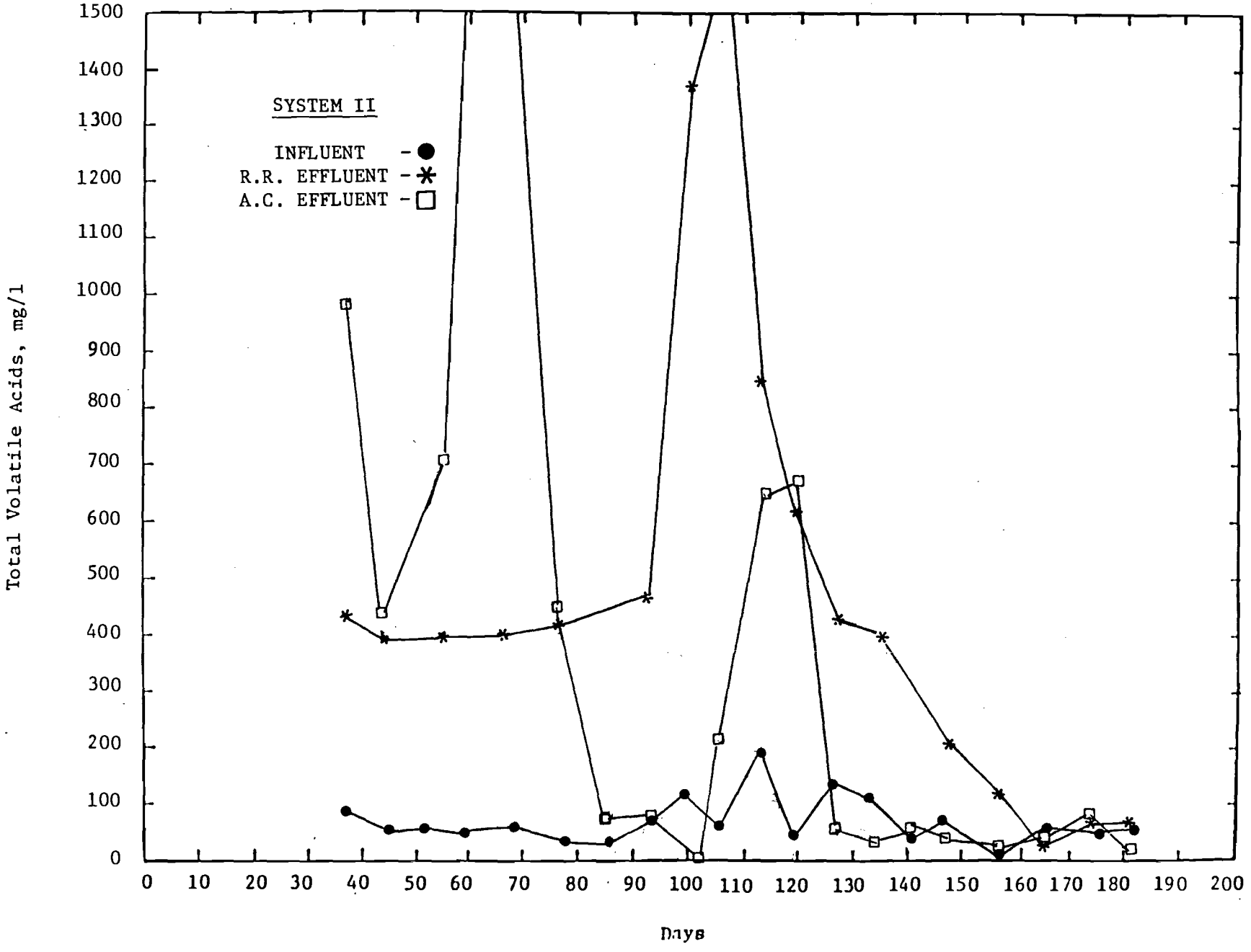

SYSTEM II
INFLUENT
R.R. EFFLUENT
A.C. EFFLUENT
Total Volatile Acids, mg/l
Days
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

Figure 4.

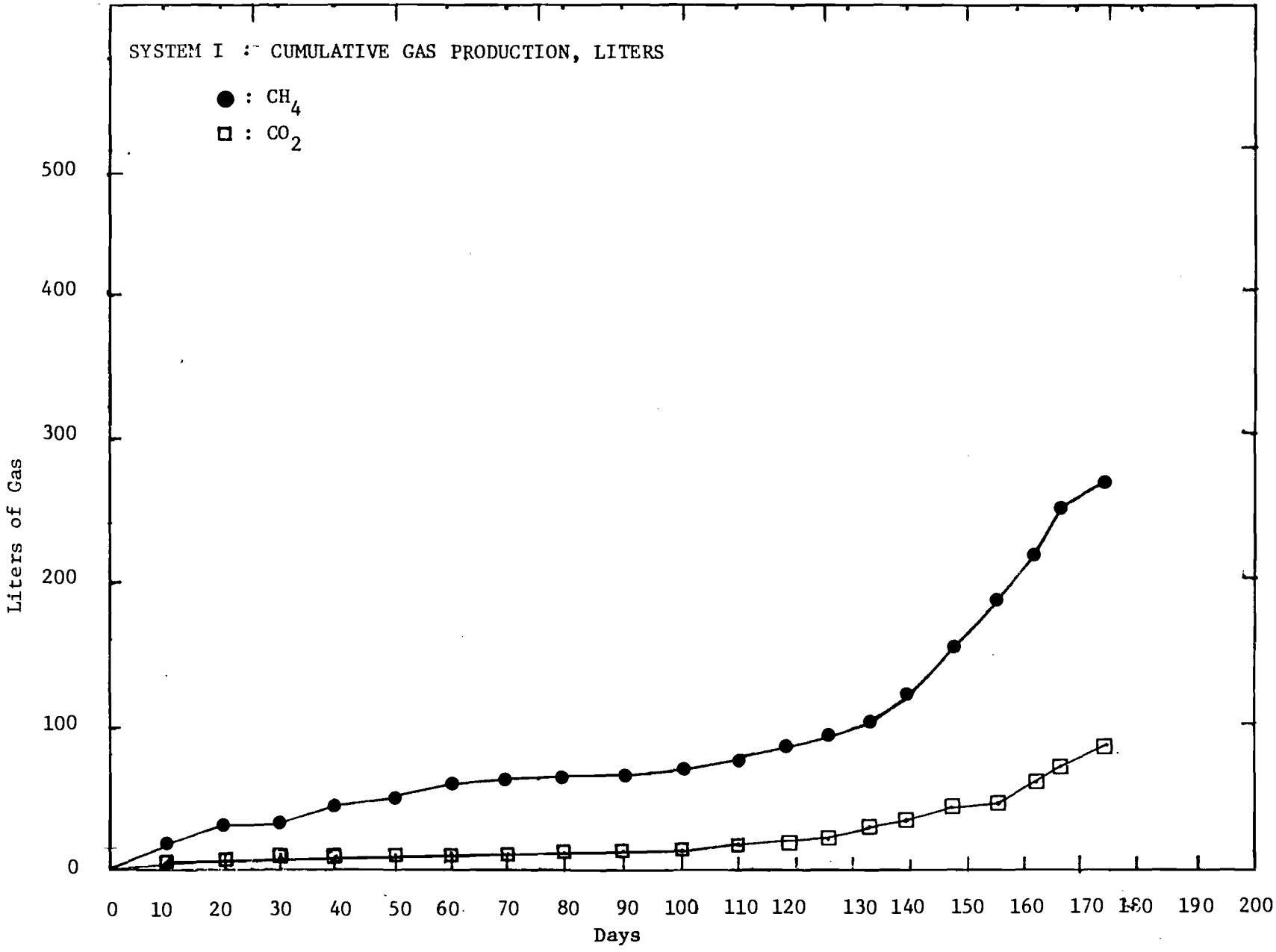

SYSTEM I : CUMULATIVE GAS PRODUCTION, LITERS
● : CH_4
□ : CO_2
Liters of Gas
0
100
200
300
400
500
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 5.

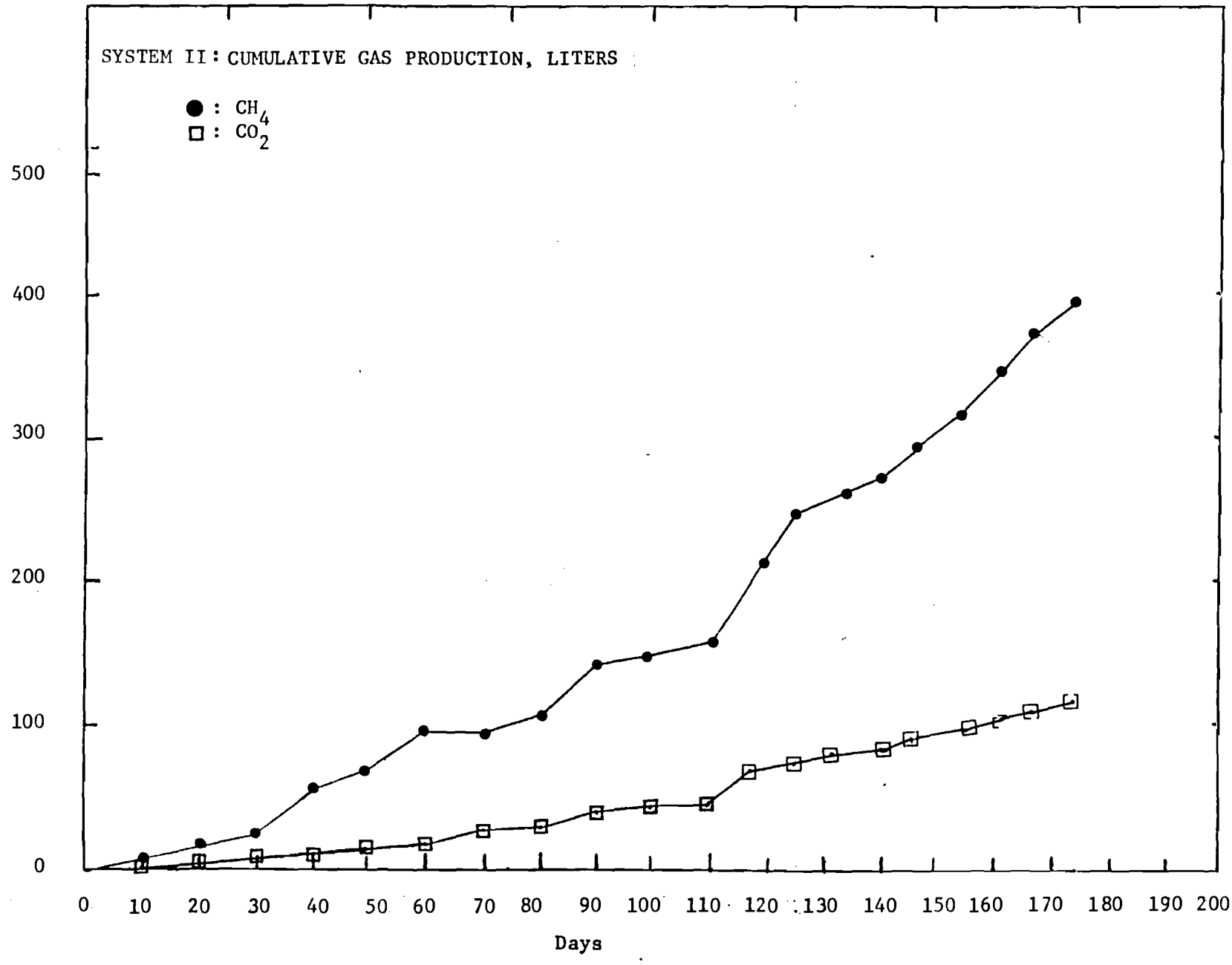

SYSTEM II: CUMULATIVE GAS PRODUCTION, LITERS
● : CH_4
□ : CO_2
Liters of Gas Produced
0
100
200
300
400
500
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 6.

1.20 ℓ/d CO_2 and 5.70 ℓ/d CH_4 for System I and 1.02 ℓ/d CO_2 and 3.58 ℓ/d CH_4 for System II. The decreasing gas production during this period is attributed to the change in overall loading to this system on day 147.

The quantity of methane being produced by System I is slightly in excess of the amount expected from the anaerobic degradation of phenol, approximately 0.2 to 0.3 of liter per day in excess of the calculated amount while System II is producing approximately 1 ℓ/day less methane than would be expected.

In System I 89% of the CH_4 is being generated in the activated carbon column while in System II 83% of the CH_4 is being generated in the activated carbon column. All of the gaseous carbon dioxide in both systems is being generated in the activated carbon columns.

4. Phenol Removal

Both Systems are continuing to remove phenol (Figures 7 & 8) with an overall removal efficiency in excess of 90%. Removal efficiencies have continuously increased to values of 93% for System II until day 147 when the anaerobic phenol effluent supplement was terminated and the loading rate on both systems was increased. At that time phenol removal efficiencies decreased for a period of approximately two weeks and have started to increase again. The bulk of the phenol is being removed in the activated carbon column with only 10 to 20% being removed in the Raschig Ring Column. Phenol removal efficiencies should continue to improve as the system attains pseudo-steady state operation.

5. TOC and COD Removals

Both System I and II are showing similar TOC and COD removal efficiencies. Influent and effluent TOC and COD values are shown in Figures 9, 10, 11 and 12. System II removal efficiencies for both TOC and COD are somewhat better than System I. TOC removals averaging 73.0% and 78.1% for Systems I & II, respectively while COD removals are 77.6% for System I and 87.1% for System II.

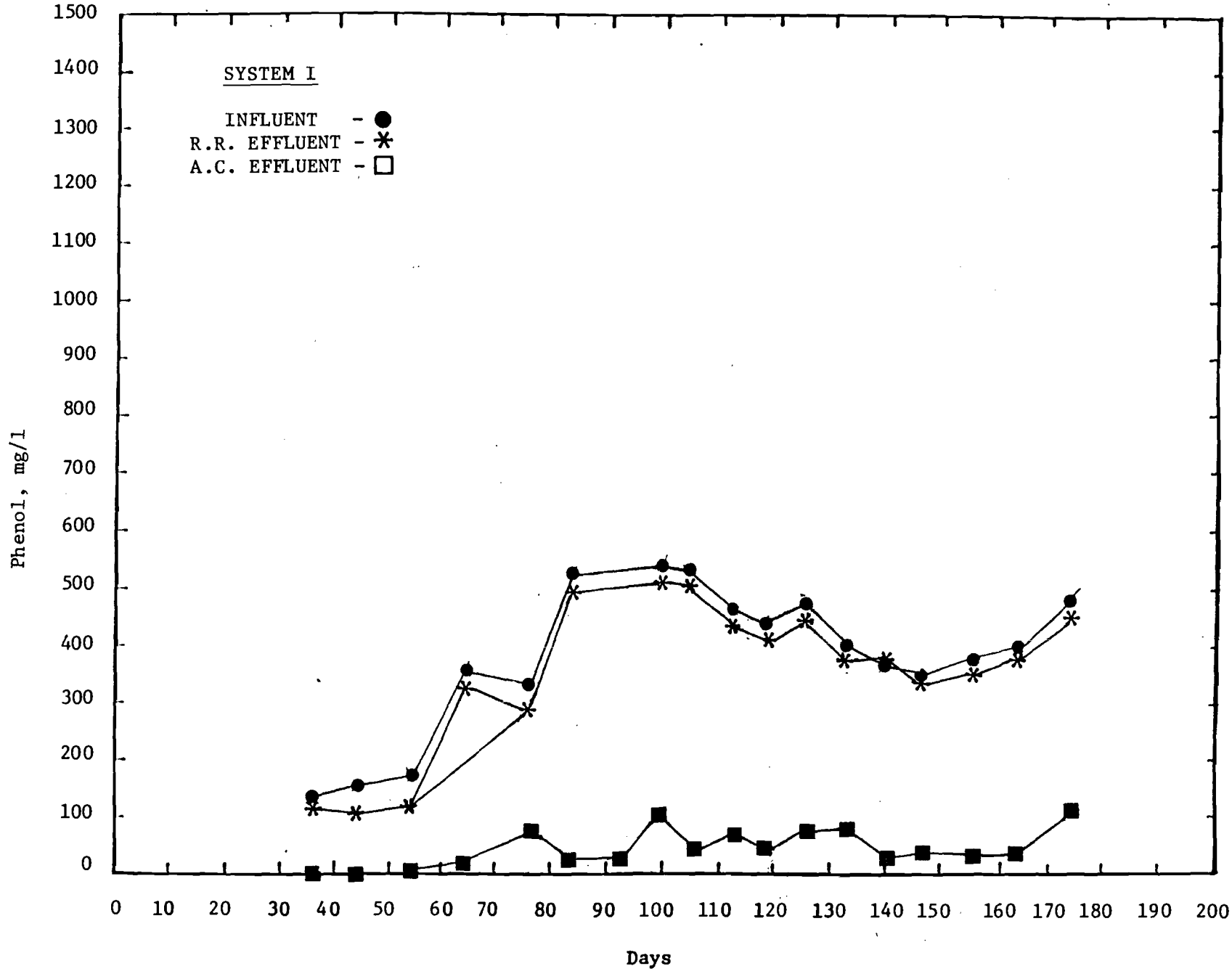

SYSTEM I
INFLUENT - ●
R.R. EFFLUENT - *
A.C. EFFLUENT - □
Phenol, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 7.

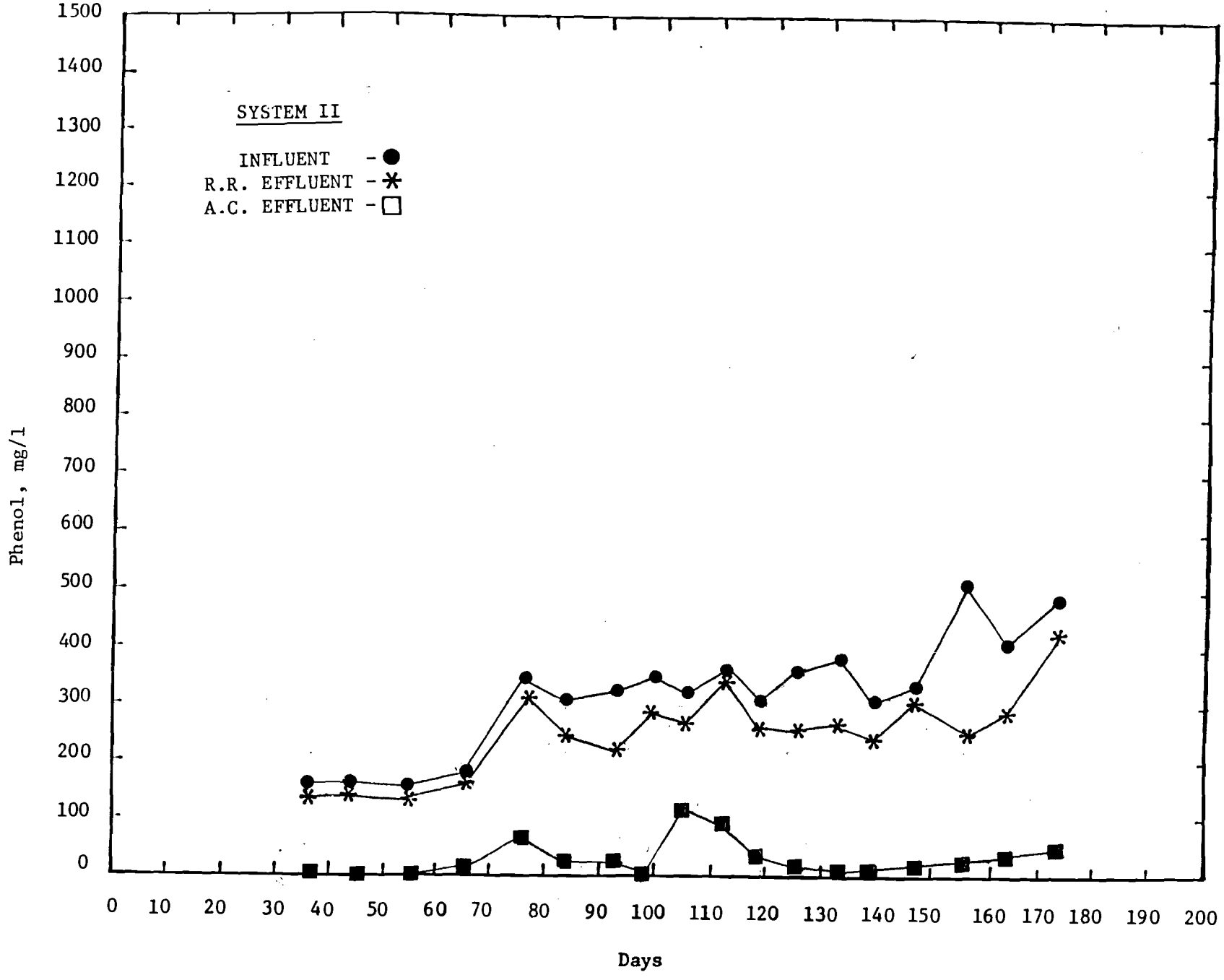

SYSTEM II
INFLUENT
R.R. EFFLUENT
A.C. EFFLUENT
Phenol, mg/l
Days
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Figure 8.

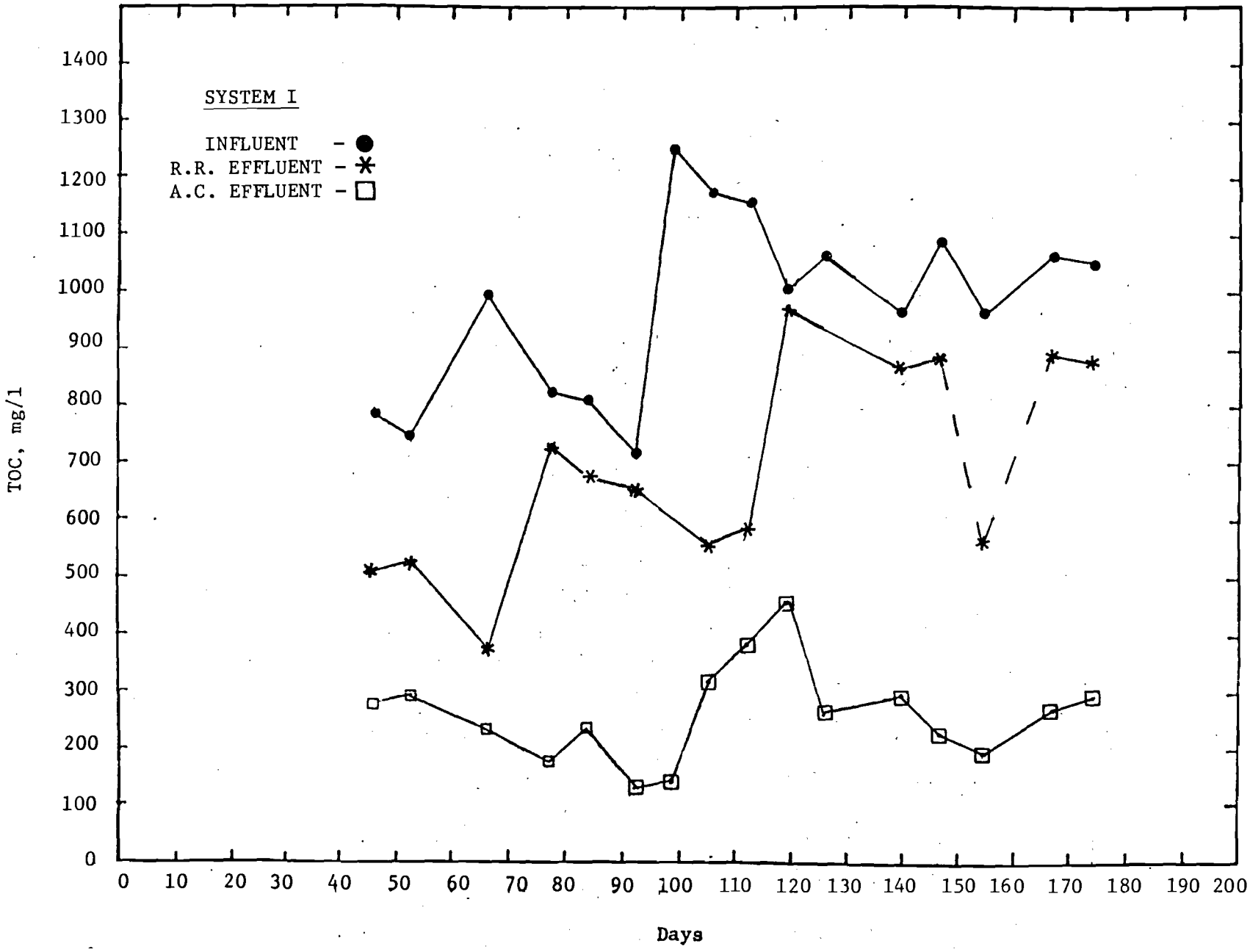

SYSTEM I
INFLUENT
R.R. EFFLUENT
A.C. EFFLUENT
TOC, mg/l
Days
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Figure 9.

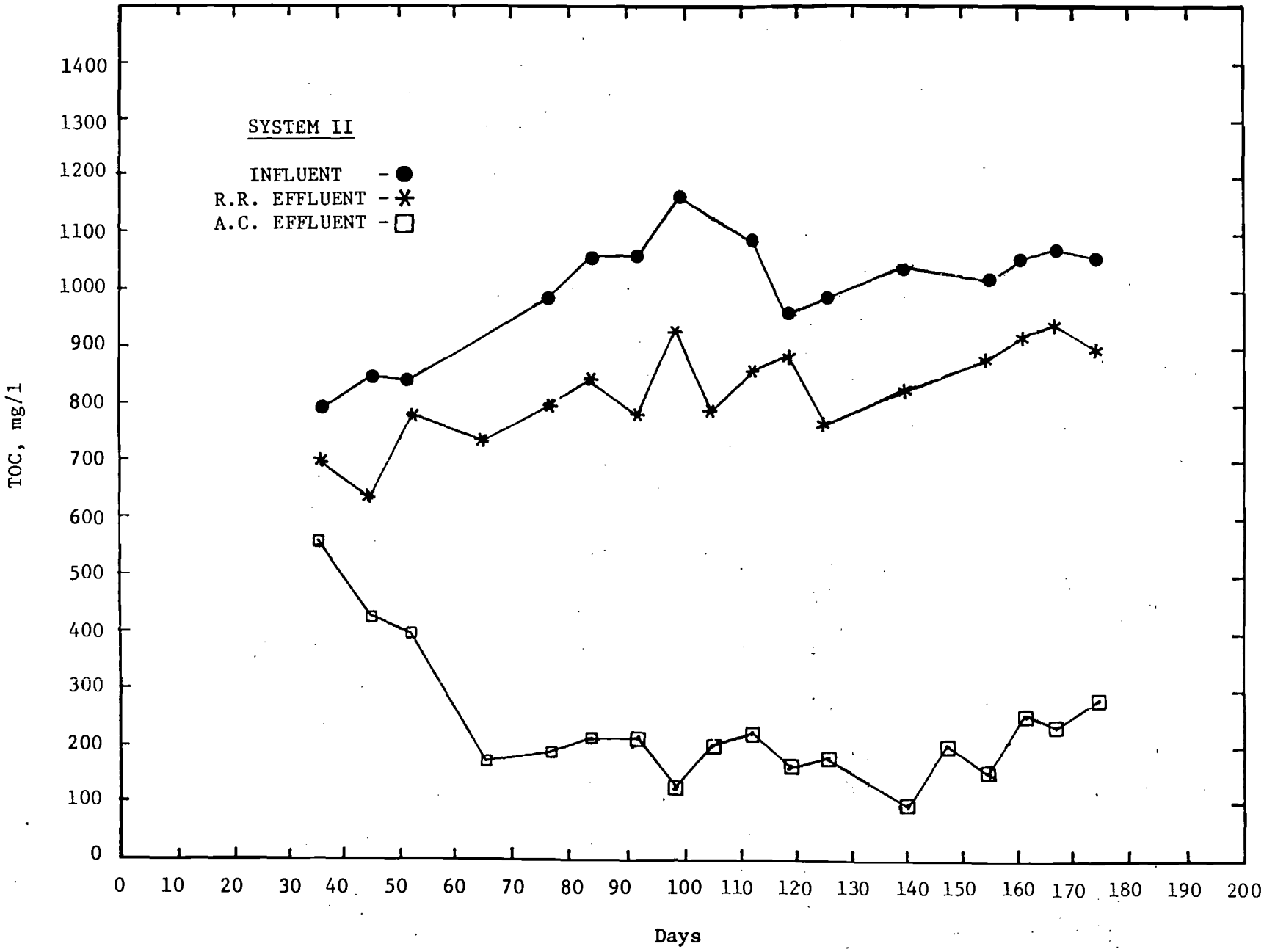

SYSTEM II
INFLUENT
R.R. EFFLUENT
A.C. EFFLUENT
TOC, mg/l
Days
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

Figure 10.

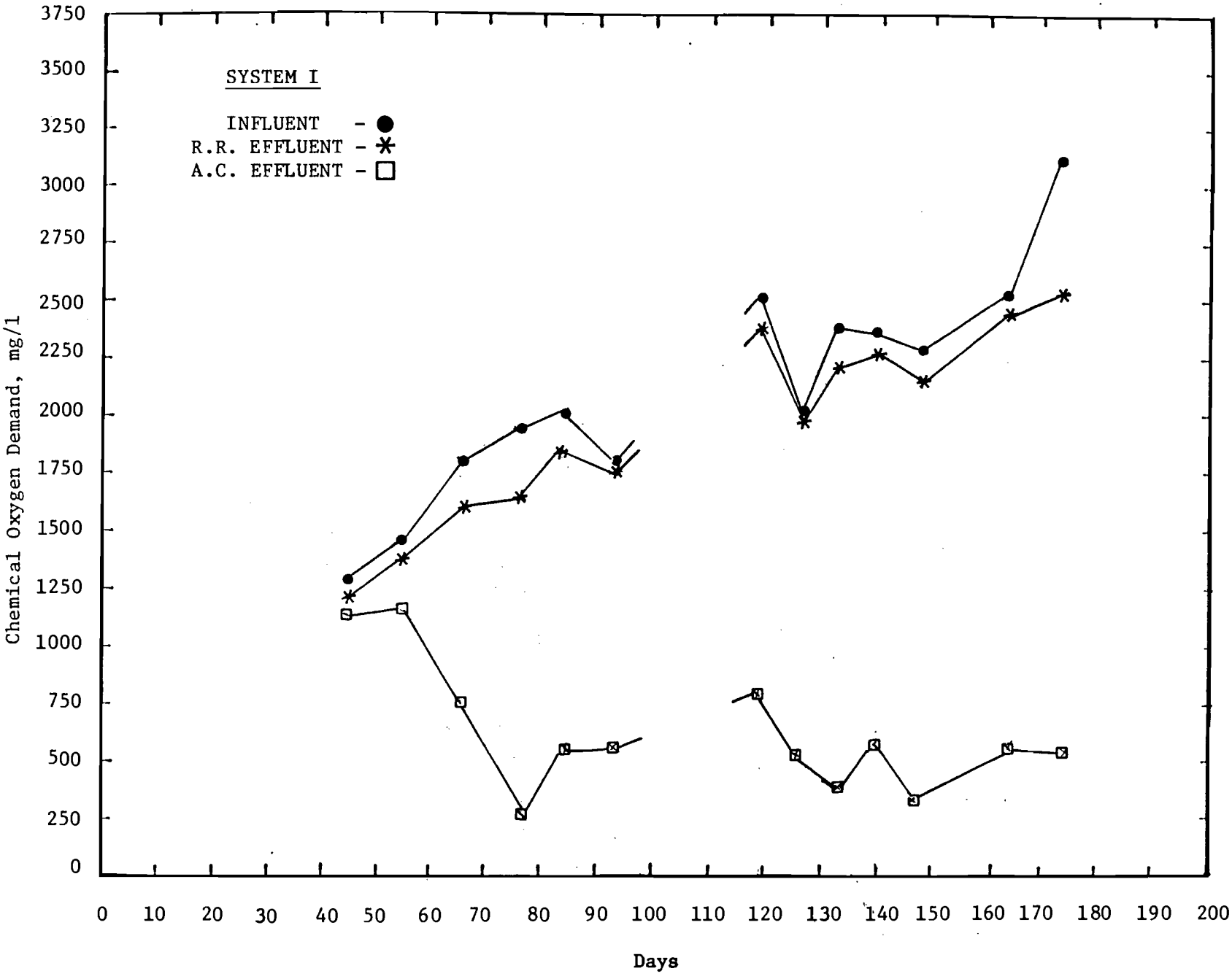

SYSTEM I
INFLUENT -
R.R. EFFLUENT -
A.C. EFFLUENT -
Chemical Oxygen Demand, mg/l
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 11.

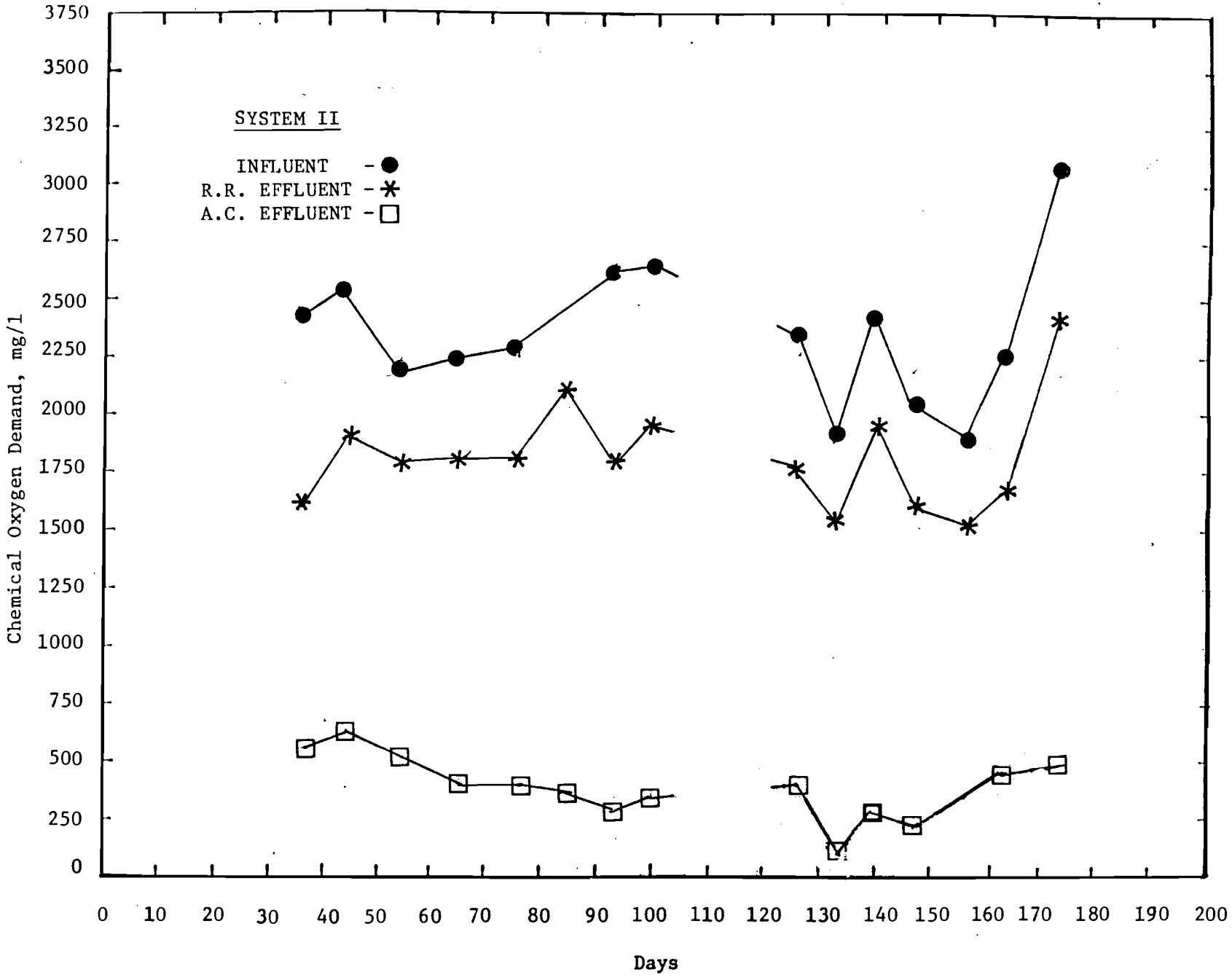

SYSTEM II
INFLUENT
R.R. EFFLUENT
A.C. EFFLUENT
Chemical Oxygen Demand, mg/l
Days
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Figure 12.

6. pH, Alkalinity and ORP

The pH of the diluted wastewater influent for both systems is in the range of 8.3 to 8.9 and decreases to 8.1 to 8.3 in the effluent from the Raschig Ring column and decreases further to 7.3 to 7.8 in the effluent from the activated carbon column.

Alkalinity values decrease slightly across the system from approximately 2400 mg/ℓ in the influent to 2100 mg/ℓ in the final effluent.

ORP values also decrease across the system from a range of -100mv to -150mv in the influent to -320mv to -360mv in the effluent from the activated carbon column.

B. System III

1. Operation and Acclimation

System III has been operated for a total period of 90 days using a 10 ml/min flow rate and a feed composition as outlined in Table 2.

2. Volatile Acid Production

Volatile acid concentrations (Figure 13) have increased as the acid forming microbial population has become established and then decreased as the methanogenic population has started to utilize them for methane formation

3. Gas Production

Production of CH_4 and CO_2 have both continuously increased (Figure 14) indicating the establishment of a viable methanogenic population of organisms in the system. CO_2 and CH_4 are being produced in both the Raschig Ring and activated carbon columns in similar quantities.

4. Phenol Removal

Phenol removal (Figure 15) is averaging 84 per-cent with approximately 12 per-cent being removed by the Raschig Ring column and the remainder by the activated carbon column.

5. TOC and COD Removals

TOC and COD removals (Figures 16 & 17) are still quite low averaging only 63% and 72%, respectively. This is due to the large concentration of volatile acids remaining in the final effluent. These removal efficiencies will improve as the system acclimates and the acids are converted to CH_4 and CO_2.

6. pH, Alkalinity, ORP

pH across the system is relatively constant with the influent having values in the range 6.8 to 6.9 and the final effluent a value of 7.1.

The alkalinity increases somewhat across the system with the influent having an average value of 1400 mg/ℓ while the effluent has a value of 1800 mg/ℓ.

TABLE II. Feed Solution For System III

Days of Operation	Feed Solution
1-49	Raw Wastewater (500 ppm TOC), Glucose (500 ppm TOC), Phosphates
49-83	Raw Wastewater (600 ppm TOC), Glucose (400 ppm TOC), Phosphates
83-90	Raw Wastewater (700 ppm TOC), Glucose (300 pp, TOC), Phosphates

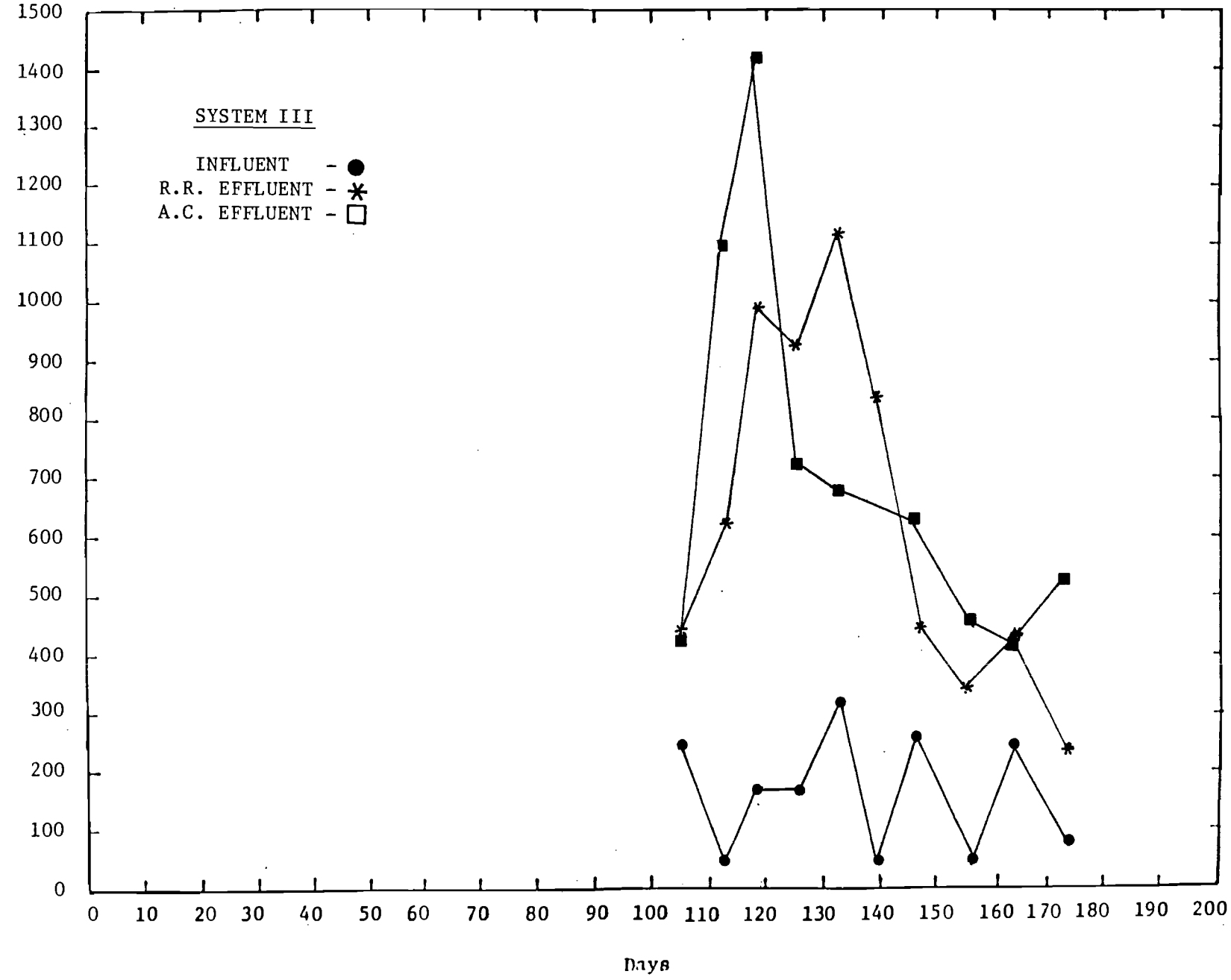

SYSTEM III
INFLUENT - ●
R.R. EFFLUENT - ✱
A.C. EFFLUENT - □
Total Volatile Acids, mg/l
Days
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Figure 13.

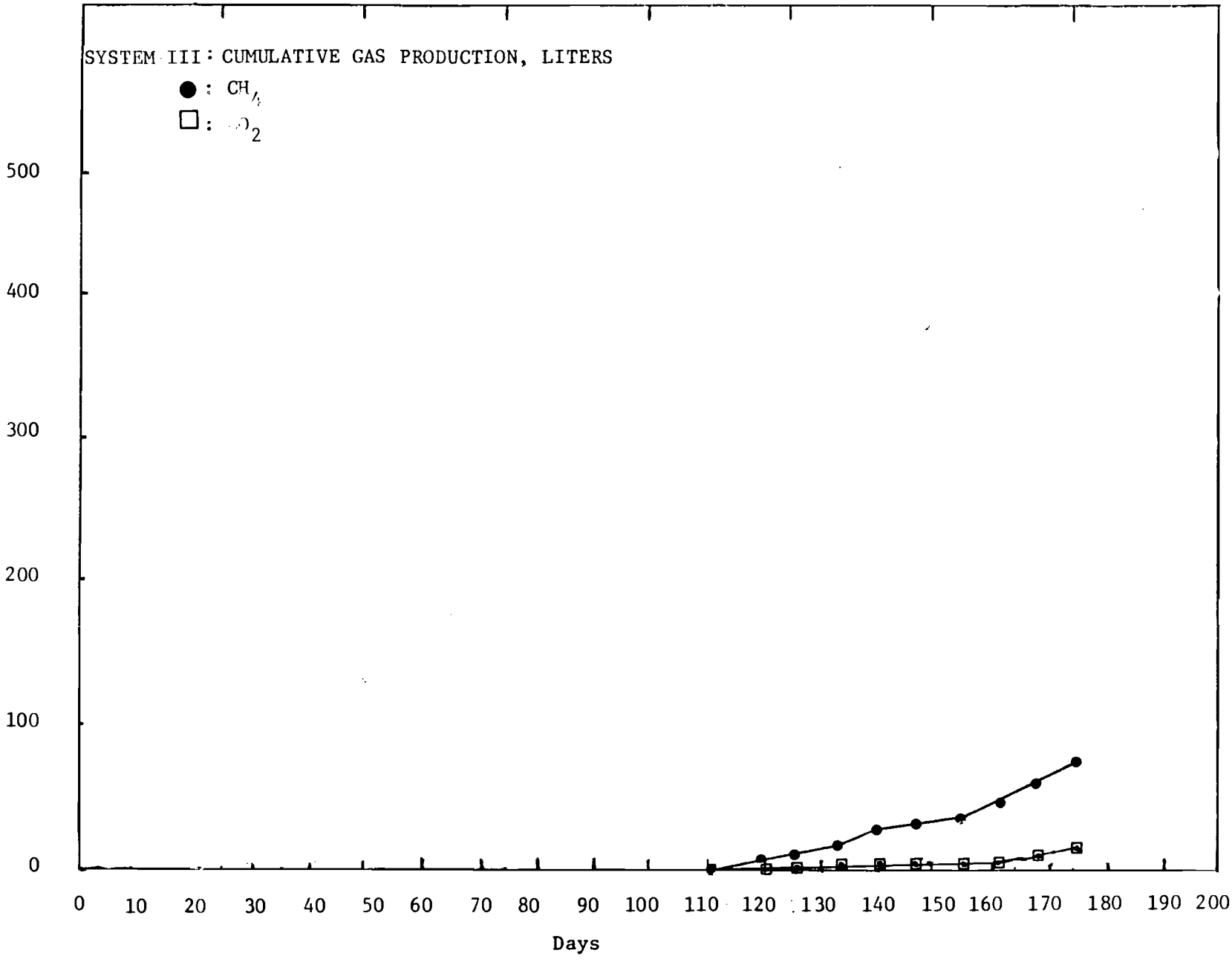

SYSTEM III: CUMULATIVE GAS PRODUCTION, LITERS
● : CH_4
□ : CO_2
Liters of Gas Produced
0
100
200
300
400
500
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 14.

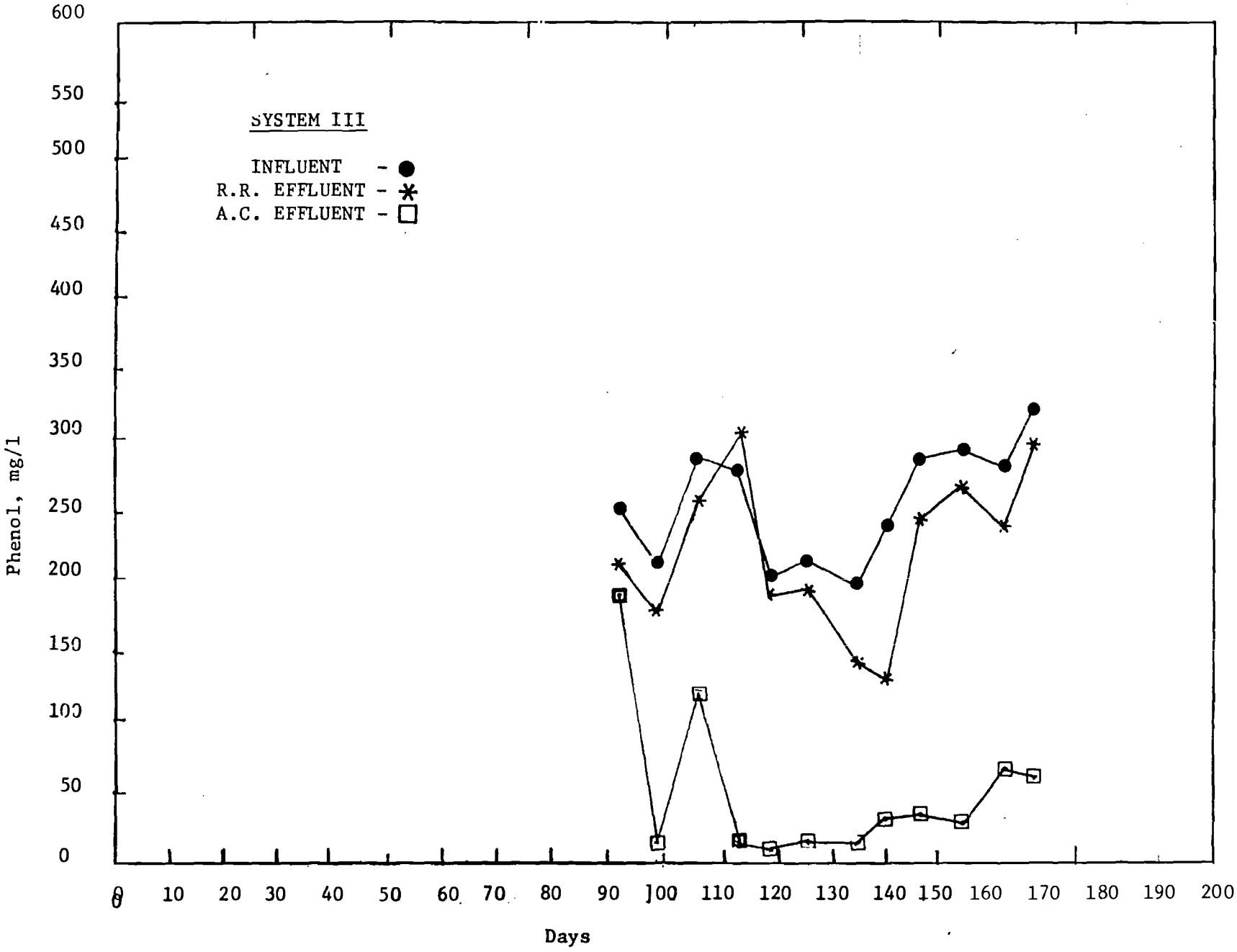

SYSTEM III
INFLUENT - ●
R.R. EFFLUENT - ✱
A.C. EFFLUENT - □
Phenol, mg/l
600
550
500
450
400
350
300
250
200
150
100
50
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 15.

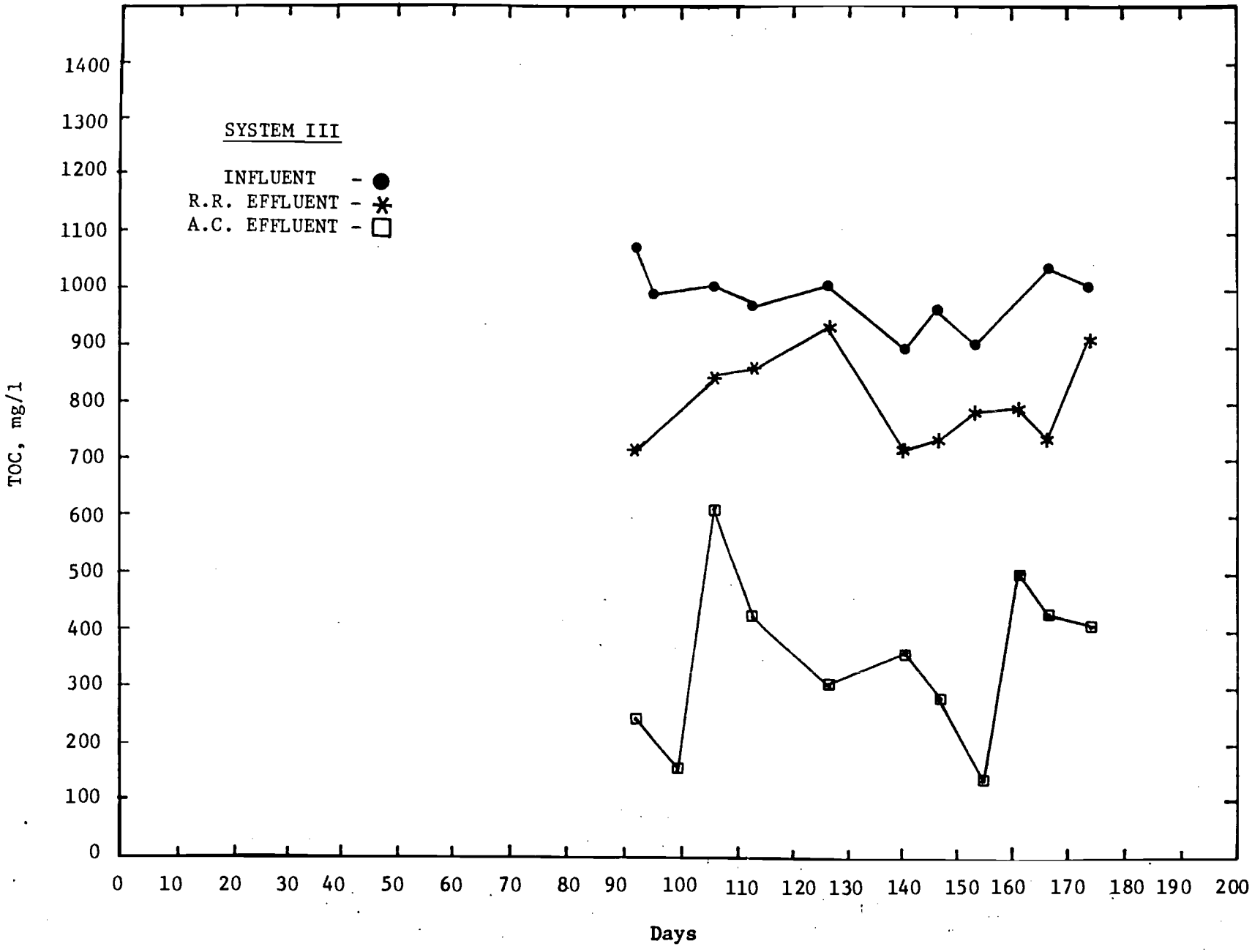

SYSTEM III
INFLUENT -
R.R. EFFLUENT -
A.C. EFFLUENT -
TOC, mg/l
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 16.

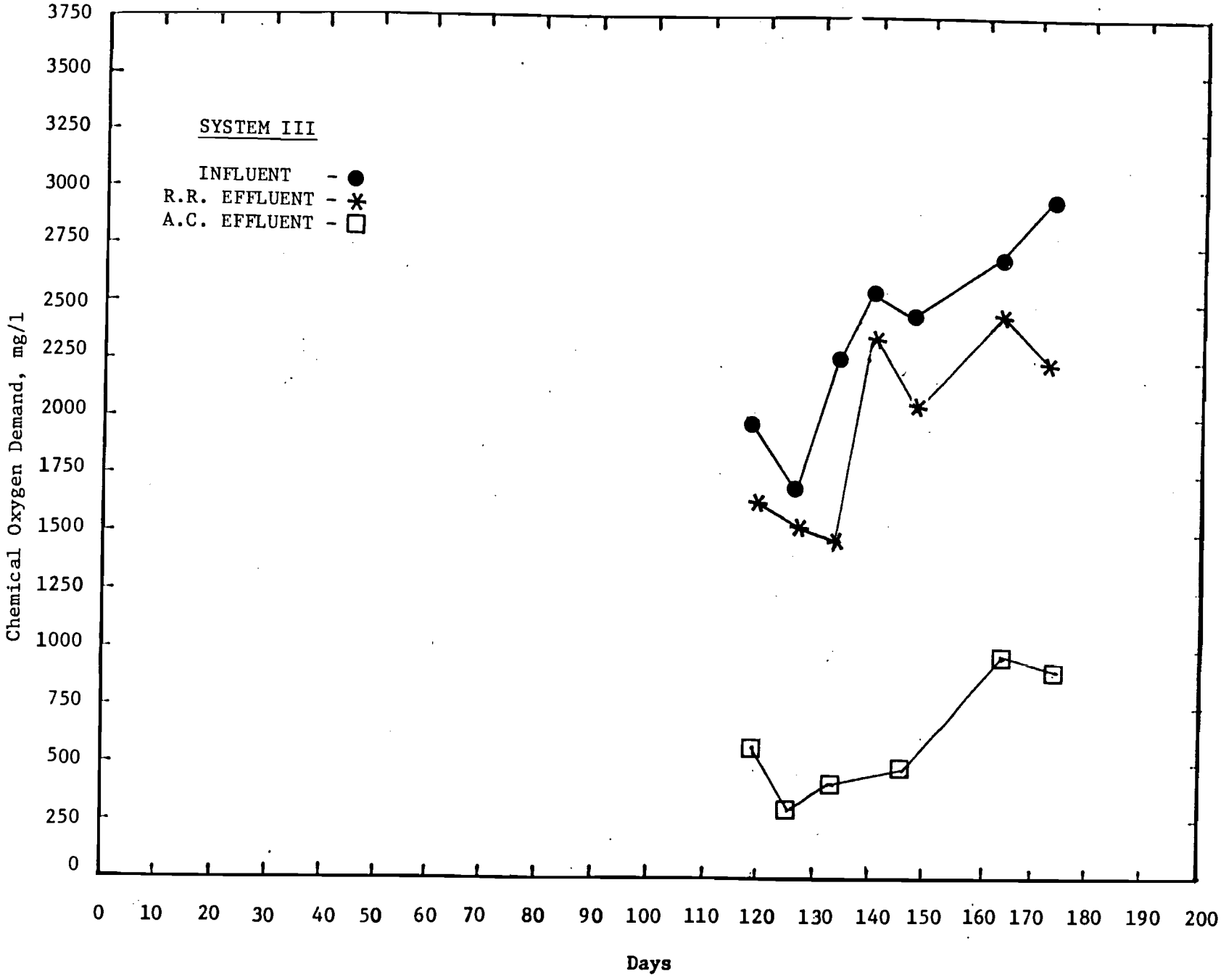

SYSTEM III
INFLUENT -
R.R. EFFLUENT -
A.C. EFFLUENT -
Chemical Oxygen Demand, mg/l
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Days

Figure 17.

ORP values decrease across the system from -170mv in the influent to -340mv in the Raschig Ring column and -265mv in the activated carbon columns.

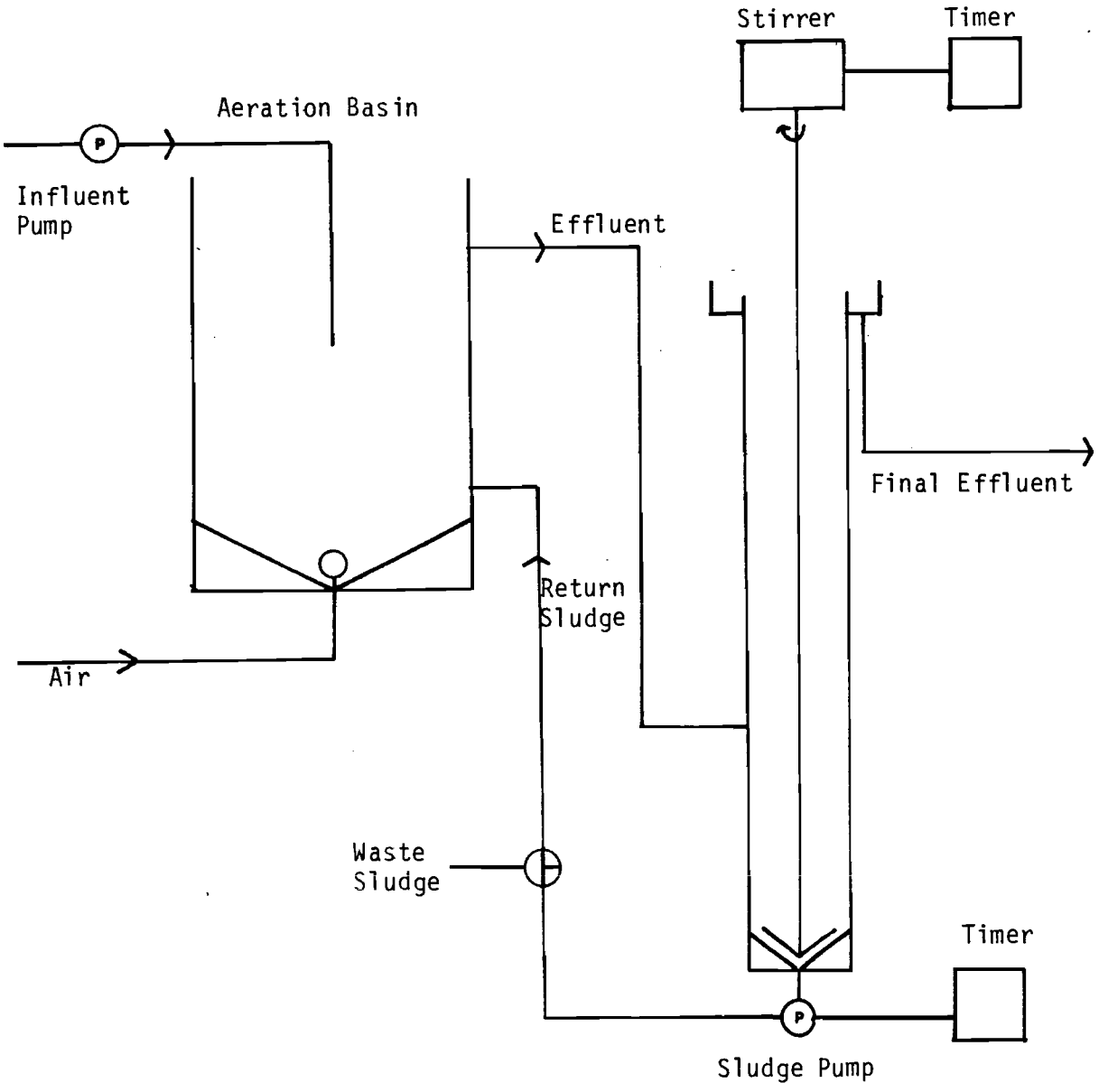

Stirrer
Timer
Aeration Basin
Influent
Pump
Effluent
Final Effluent
Return
Sludge
Air
Waste
Sludge
Timer
Sludge Pump

Figure 18.

III. NITRIFICATION SYSTEM

A. Introduction

A bench scale activated sludge system consisting of an aeration basin, clarifier and associated pumps and timers has been constructed (Figure 18) and placed into continuous operation. A second aeration basin-clarifier system is available and can be used if problems develop with the first unit.

B. Acclimation and Operation

Initial acclimation was accomplished by seeding the system with a nitrifying sludge obtained from a local municipal wastewater treatment plant which operates a pure oxygen-activated sludge system. The system was operated for several days on a fill and draw basis with 10% of the aeration basin contents replaced daily. The system then was switched to a continuous flow operation. The influent to the system is the combined effluents from Anaerobic Systems I and II. The two effluents are mixed and then diluted 10 to 1 to give an influent to the nitrifying system which contains 50 mg/ℓ TOC, 100 mg/ℓ COD, and 63 mg/ℓ NH_3-N.

The influent is pumped to the aeration basin at a rate of 10 ml/min giving a hydraulic residence time of approximately 18 hours. The overflow from the aeration basin flows to the clarifier where the suspended solids settle. The sludge is then periodically pumped back to the aeration basin. Alkalinity and pH are being maintained by manually adding Na_2CO_3 to the system at the present time.

C. Results

The results to date are very encouraging. Effluent NH_3-N values are less than 1 mg/ℓ giving removal efficiencies of greater than 98%. Influent NO_3^--N values are quite low, less than 1 mg/ℓ while effluent values are in the range of 50 to 60 mg/ NO_3^--N.

COD and TOC removals are quite low at this time averaging 35% and 39%, respectively.

IV. SOLVENT EXTRACTION

A. Extraction System

A three-stage solvent extraction system has been constructed (Figure 19) and is being operated to evaluate operational procedures and removal efficiencies of the system.

B. Results

Extraction of raw wastewater with MIBK using a wastewater to solvent ratio of 3 to 1 gave 90 to 95% phenol removals. Overall TOC removals have not been evaluated at this time due to the solubility of MIBK in water.

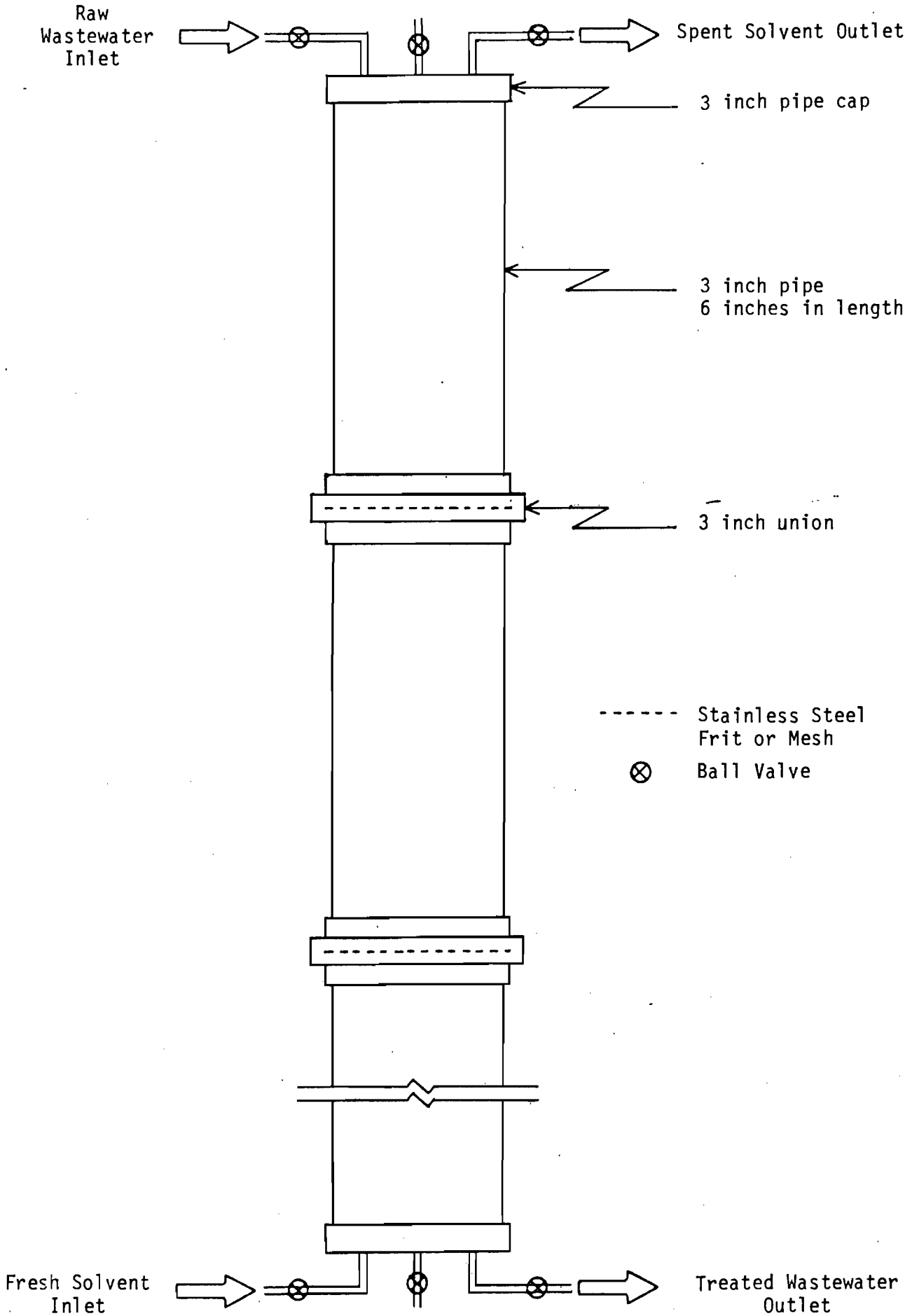

Raw
Wastewater
Inlet
Spent Solvent Outlet
3 inch pipe cap
3 inch pipe
6 inches in length
3 inch union
Stainless Steel
Frit or Mesh
Ball Valve
Fresh Solvent
Inlet
Treated Wastewater
Outlet

Figure 19.

V. AMMONIA STRIPPING SYSTEM

A. Ammonia Stripper

A stripping tower has been constructed (Figure 20) to air strip ammonia from the solvent extracted wastewater prior to biological treatment.

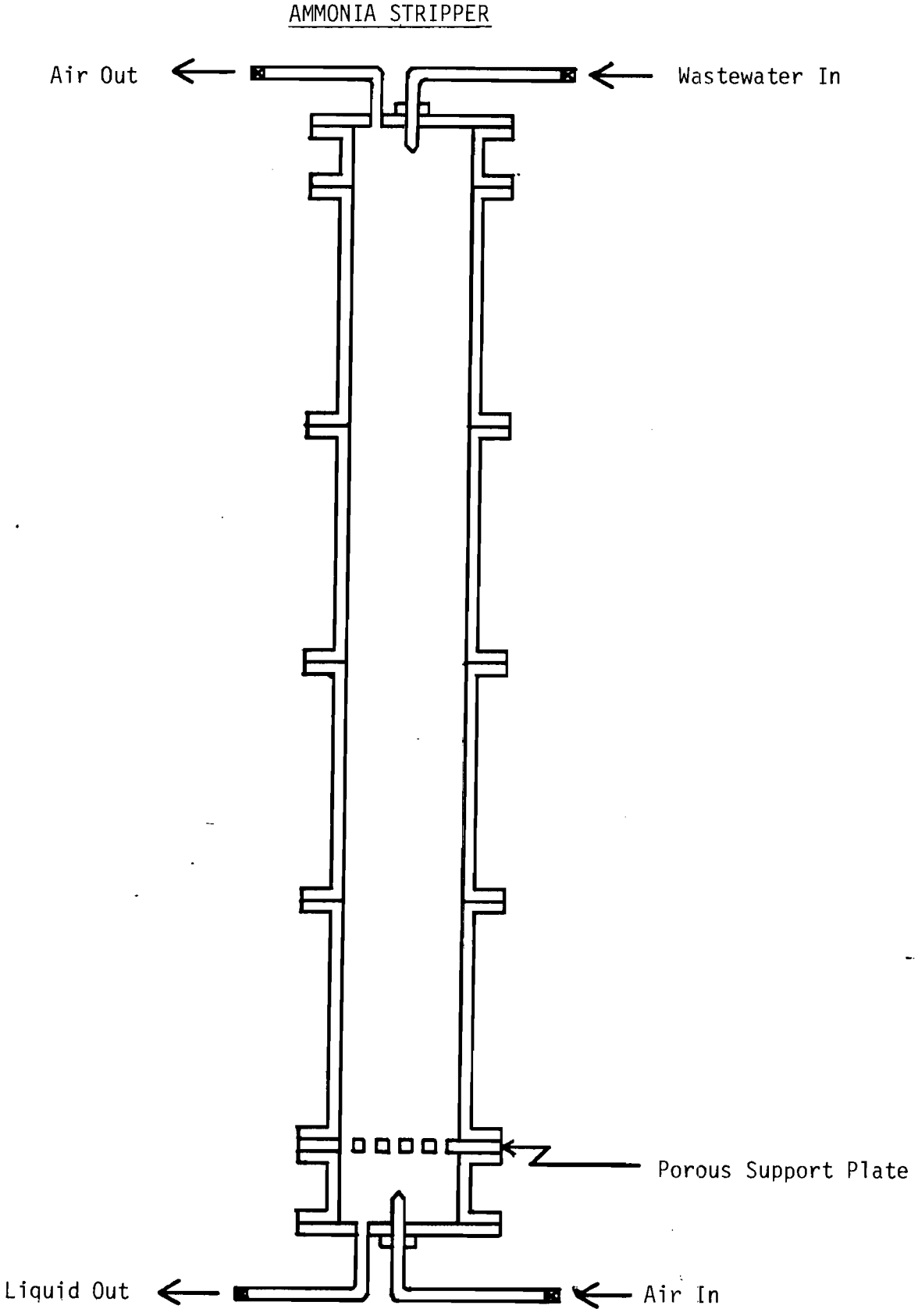

AMMONIA STRIPPER
Air Out
Wastewater In
Porous Support Plate
Liquid Out
Air In

Figure 20.

VI. FUTURE WORK

Steady state operating parameters for System I and II will be otained over the next 30 to 60 days at a fixed loading of ~1000 mg/l TOC and an influent flow of 10 ml/min. When this has been completed the loading rate (in terms of TOC) will be increased in System I by 50% (Influent TOC 1500 mg/l) and the system will be allowed to reach steady state again and be reevaluated according to the project proposal.

Acclimation of System III will continue in order to have a back up unit if inhibition or failure of either System I or II occurs.

Acclimation and increased loading of the nitrification systems will continue to determine the maximum loading rate and NH_3-N concentrations which can be sustained by the system on a continuous basis.

Solvent extraction of air stripping of large quantities of wastewater will begin and chemical evaluation of anaerobic treatment of the resulting pretreated wastewater will be undertaken.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #4
July 1982

by

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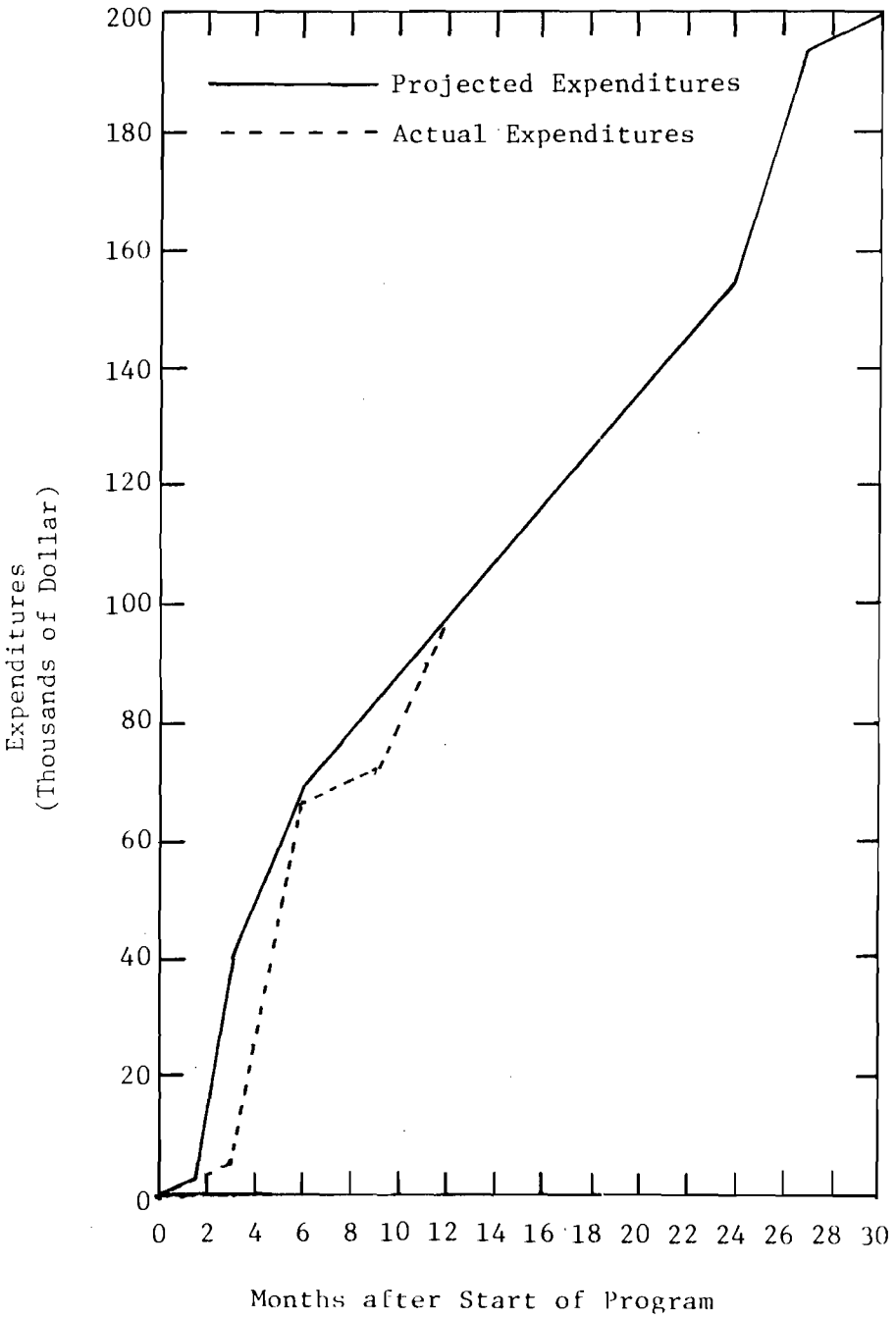


Fig. 2. Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

II. ANAEROBIC TREATMENT SYSTEMS

A. Systems I and II

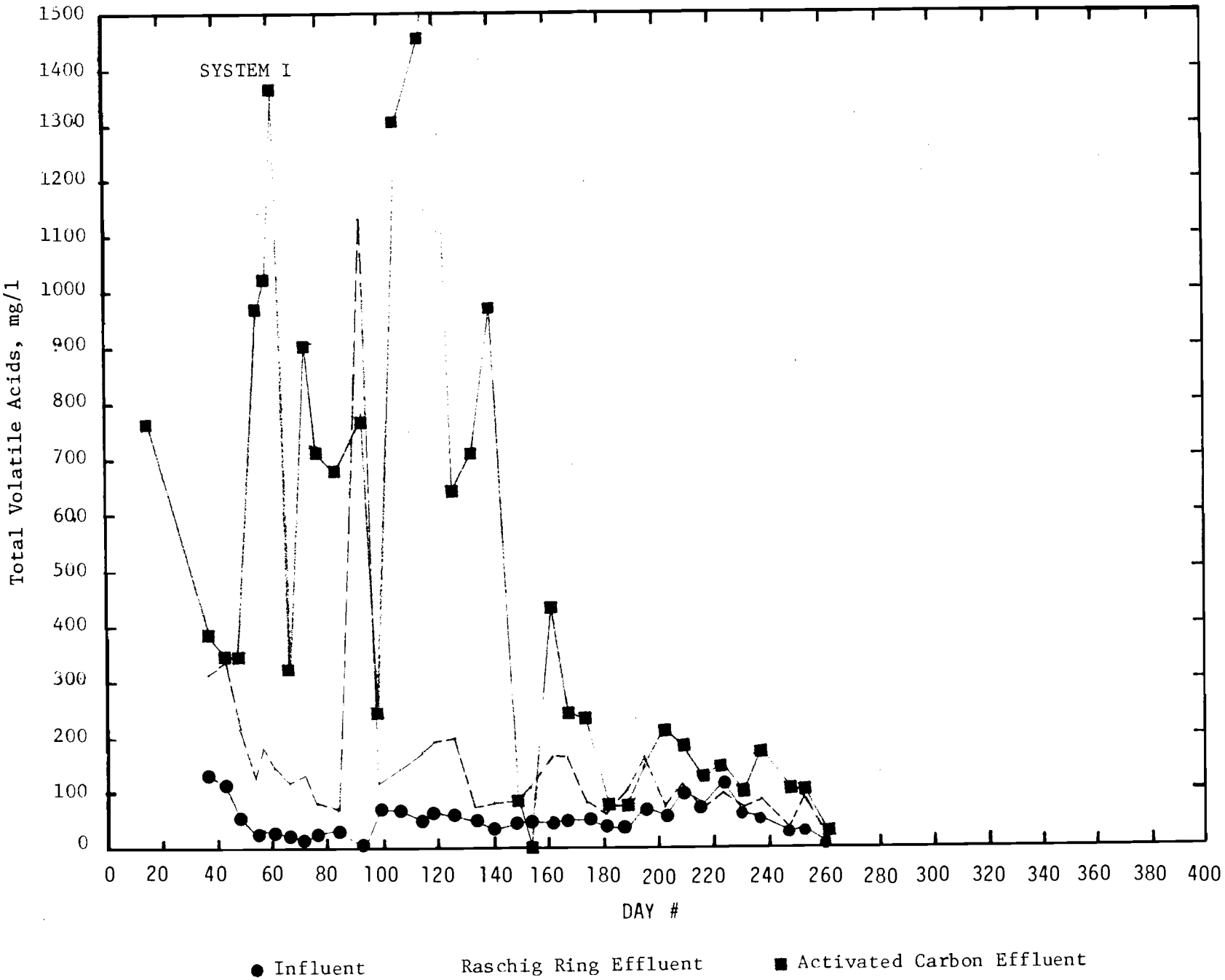
1. Operation and Loading Changes

Systems I and II have been operated since the last quarterly report for an additional period of 91 days (day 175-266). During this time System I and II received identical feed substrates of diluted wastewater and phosphates. The concentration of the wastewater was ~10% (1,000 ppm TOC) for a period of 20 days (day 175-195). On day 196 of operation the concentration of raw wastewater in the influent was increased to ~15% (1,500 ppm TOC) and the system was operated for an additional 40 days (day 126-236). During this latter period performance of both Systems I and II decreased markedly. In order to improve the efficiency of the system performance $FeCl_3$ was added to the feed substrate on day 209 to either precipitate, in the case of S^{-2}, or complex in the case of CN^- and SCN^-, potentially inhibitory species. No improvement in operation was noted. Therefore on day 237 the influent raw wastewater concentration was reduced to ~10% (100 ppm TOC) and the systems were operated an additional 17 days under these conditions. Lack of biological activity as evidenced by extremely low TOC and COD removal coupled with a lack of gas production indicated the systems were either severly inhibited or had failed. Therefore, on day 254 both Systems I and II were drained, reseeded with sludge from a municipal anaerobic sludge digester and reacclimation of these two systems was initiated.

Data obtained during the psuedo steady state operation of System I and II (day 147-195) is presented in the following sections.

2. Volatile Acid Production

Total volatile acid concentrations for influent, Raschig Ring effluent and activated carbon column effluent are shown in Figures 3 and 4. Influents concentrations averaged 45 ppm during the period from day 147-194 while the Raschig Ring


SYSTEM I
Total Volatile Acids, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
Raschig Ring Effluent
■ Activated Carbon Effluent

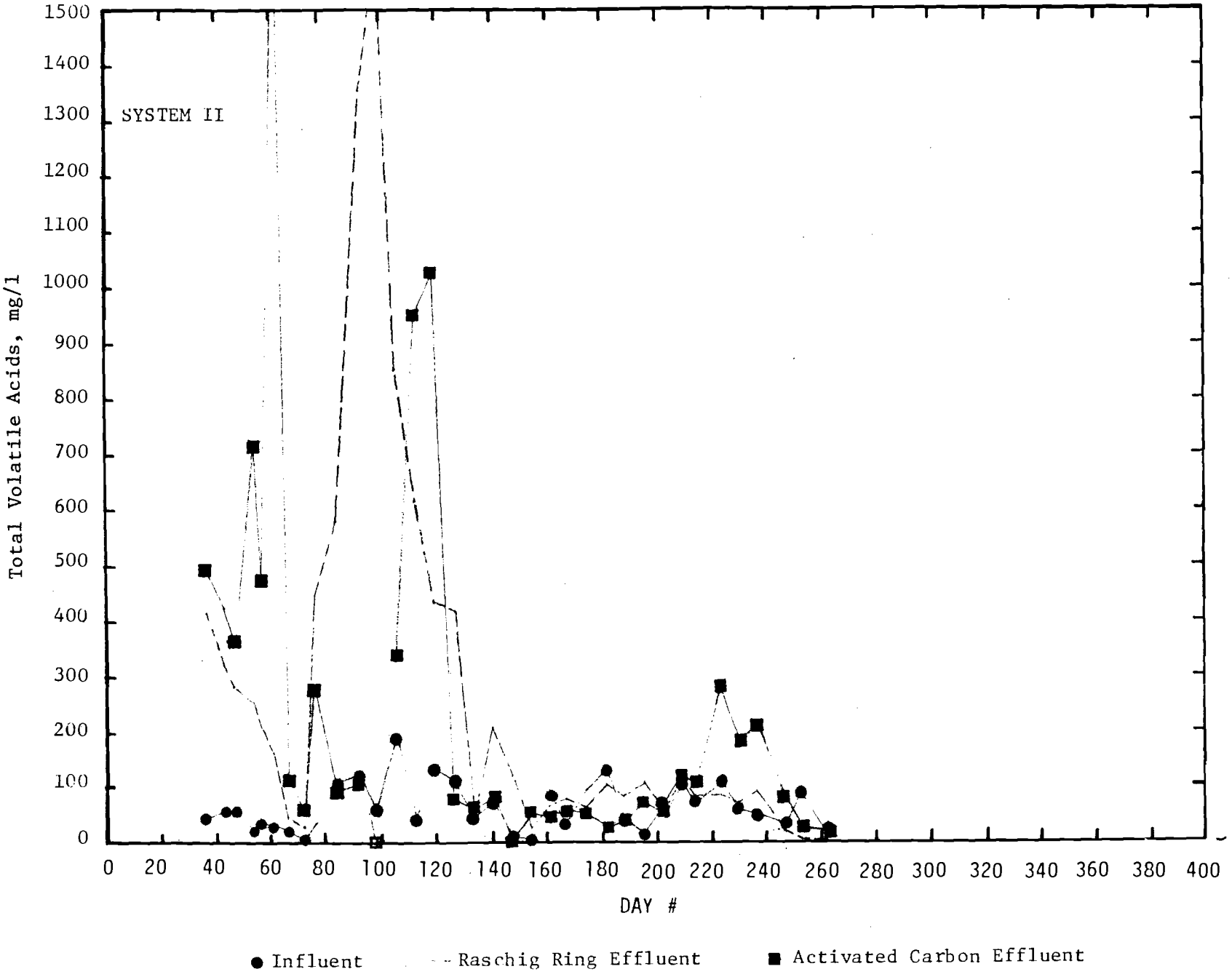

SYSTEM II
Total Volatile Acids, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
Raschig Ring Effluent
■ Activated Carbon Effluent

Figure 4

Effluent averaged 120 ppm for System I and 47 ppm for System II. Average values for effluent from the activated carbon columns were 193 ppm and 68 ppm for Systems I and II respectively.

Upon increasing the raw wastewater concentration to 15% during the period day 195-230 the total volatile acids in the influent increased to an average value of 83 ppm while the Raschig Ring Effluent concentrations were 85 ppm and 87 ppm for Systems I and II indicating virtually no conversion of substrate to volatile acids in the Raschig Ring column. Average volatile acid concentrations in the activated carbon column effluent during the same period were 150 ppm and 154 ppm for Systems I and II respectively indicating volatile acids were now being formed in the activated carbon column rather than being converted to methane.

3. Gas Production

Gas production from the two Systems is shown in Figures 5 and 6. Average daily gas production for the period day 147-194 for both systems was 1.2 ℓ/day CO_2 and 4.5 ℓ/day CH_4, with System I showing more variability in daily gas production than System II.

Upon increasing the raw wastewater concentration to 15% System I showed a decrease in gas production to a value of zero on day 202 while System II showed an increase in gas production to 5.5 ℓ/day on day 202 and then decreased to zero on day 209.

These decreases in gas production indicated a loss of bacterial activity either due to inhibition or toxicity.

4. Phenol Removal

During the period day 147-195 both Systems continued to show good phenol removal as shown in Fgiure 7 and 8 with ranges of removal efficiencies of 79-93% and 84-95% for Systems I and II, respectively. The average removal efficiency for both systems for this period has been 90%.

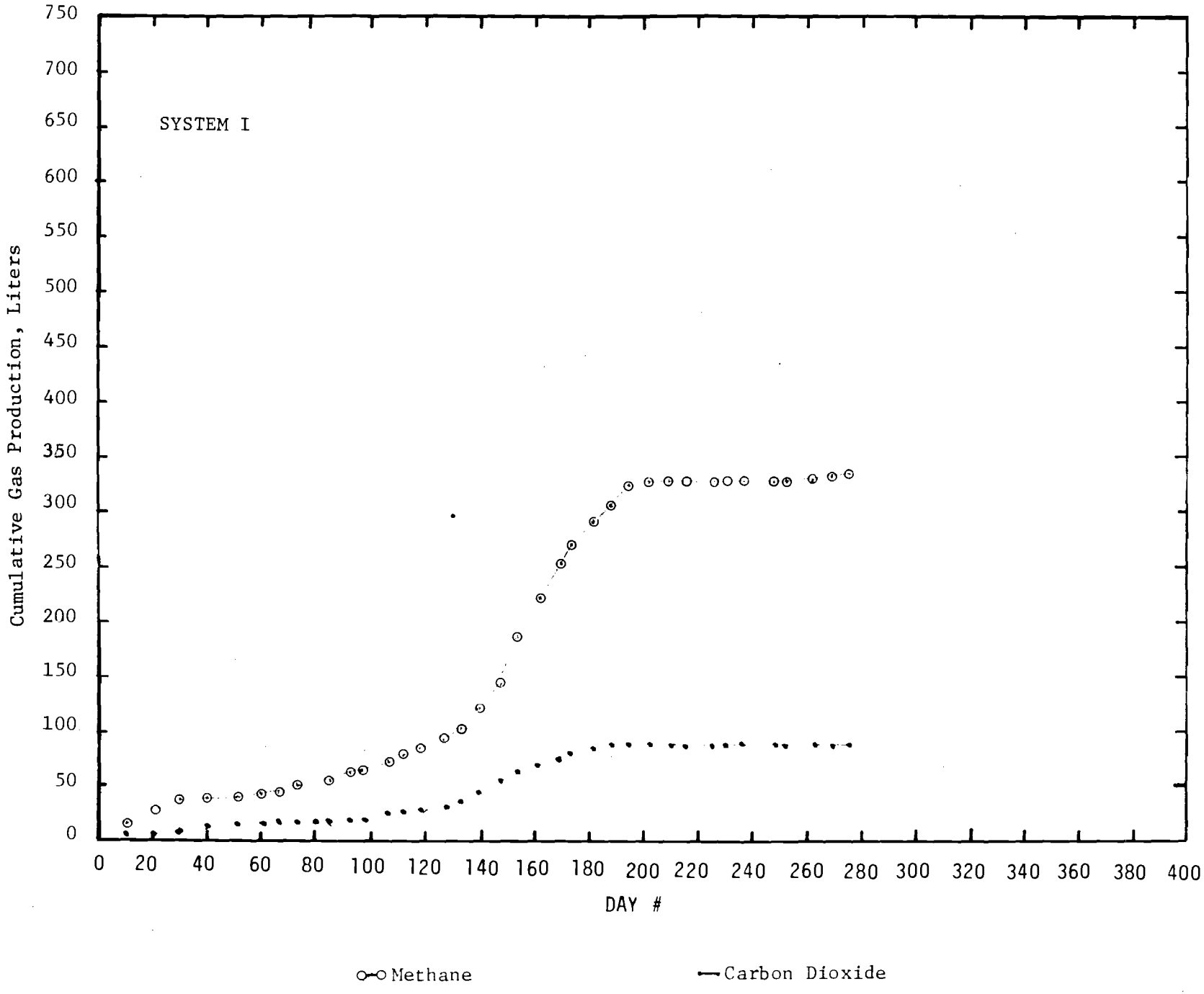
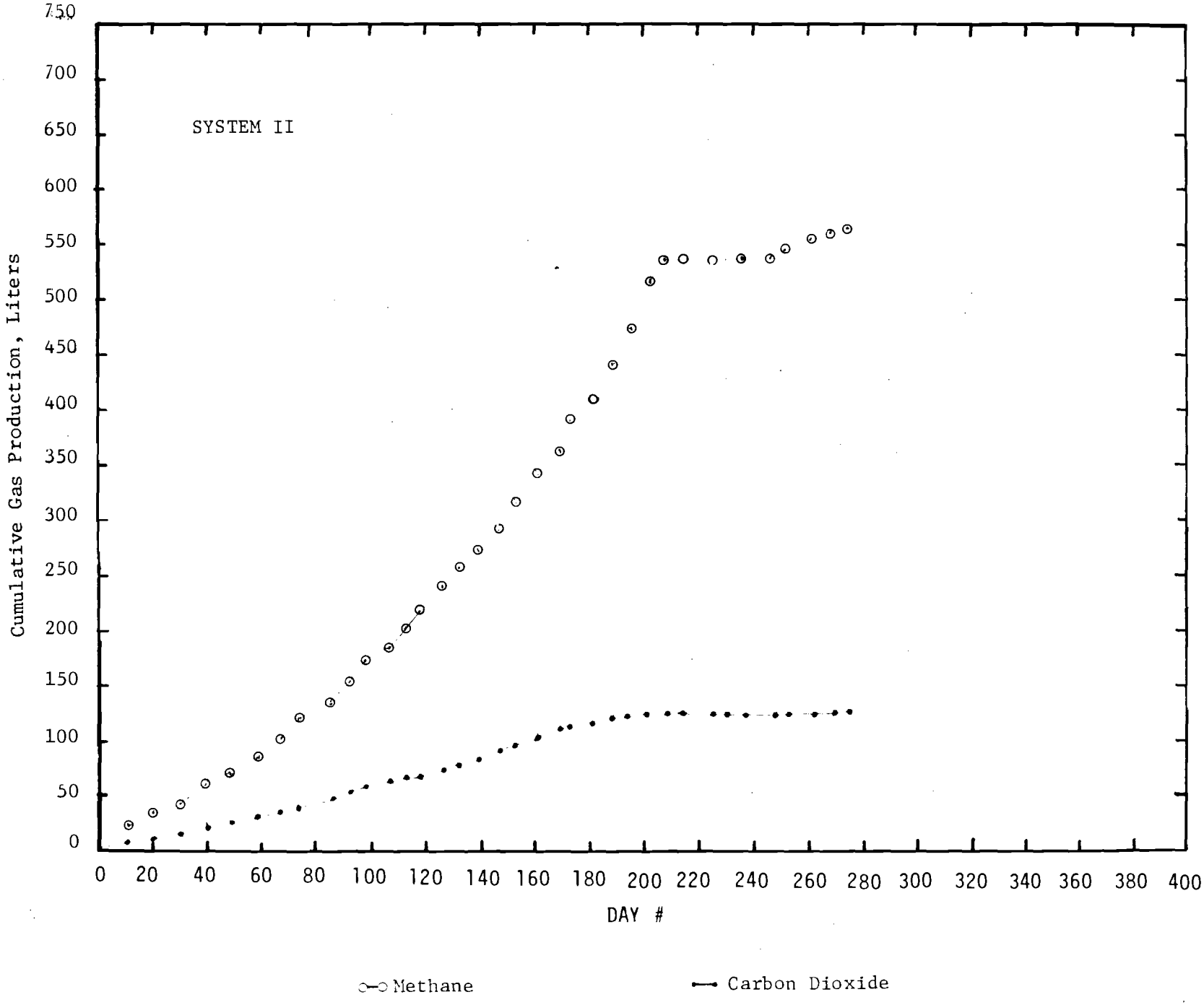

SYSTEM I
Cumulative Gas Production, Liters
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
Methane
Carbon Dioxide

Figure 5


SYSTEM II
Cumulative Gas Production, Liters
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
Methane
Carbon Dioxide

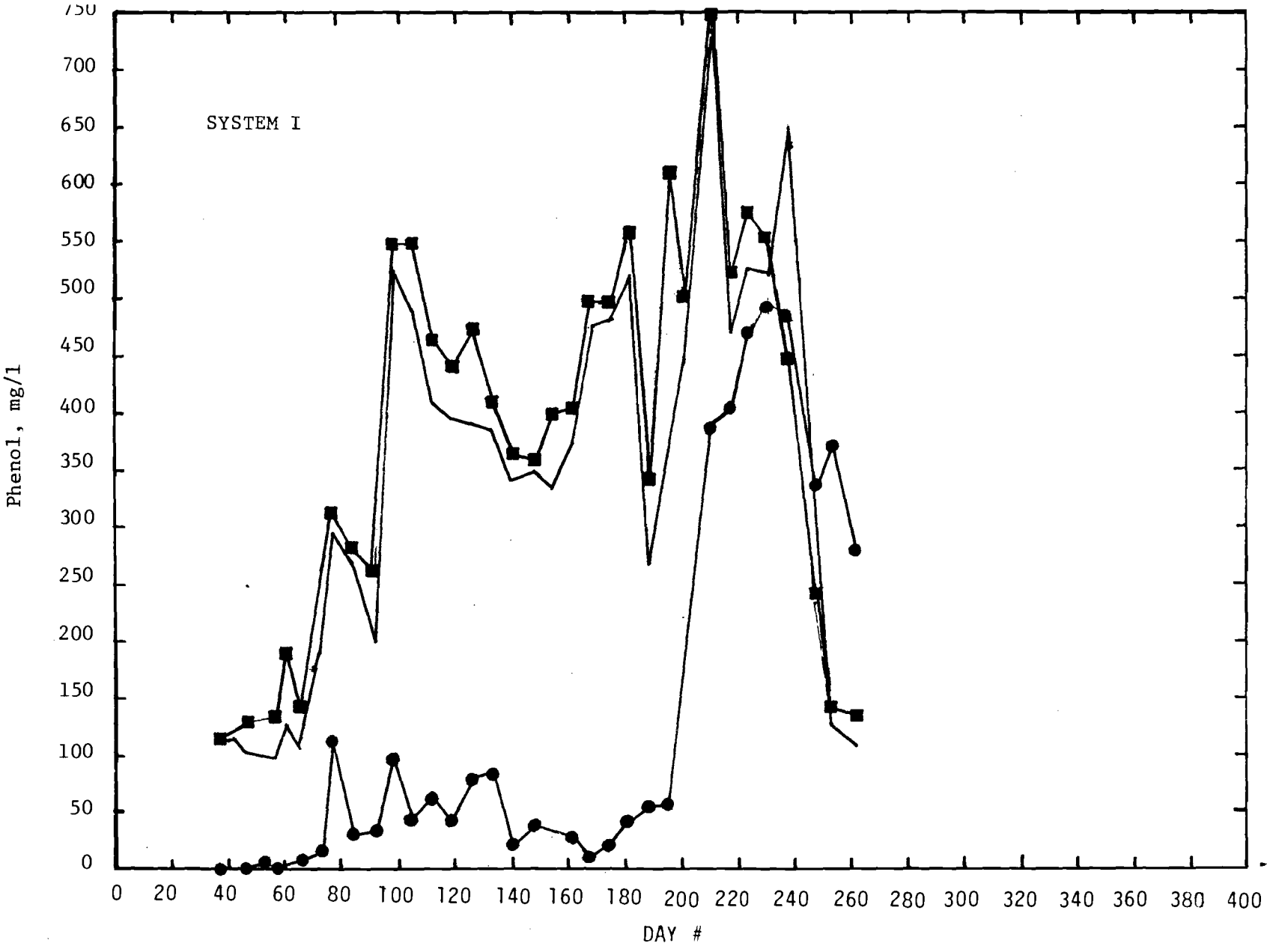
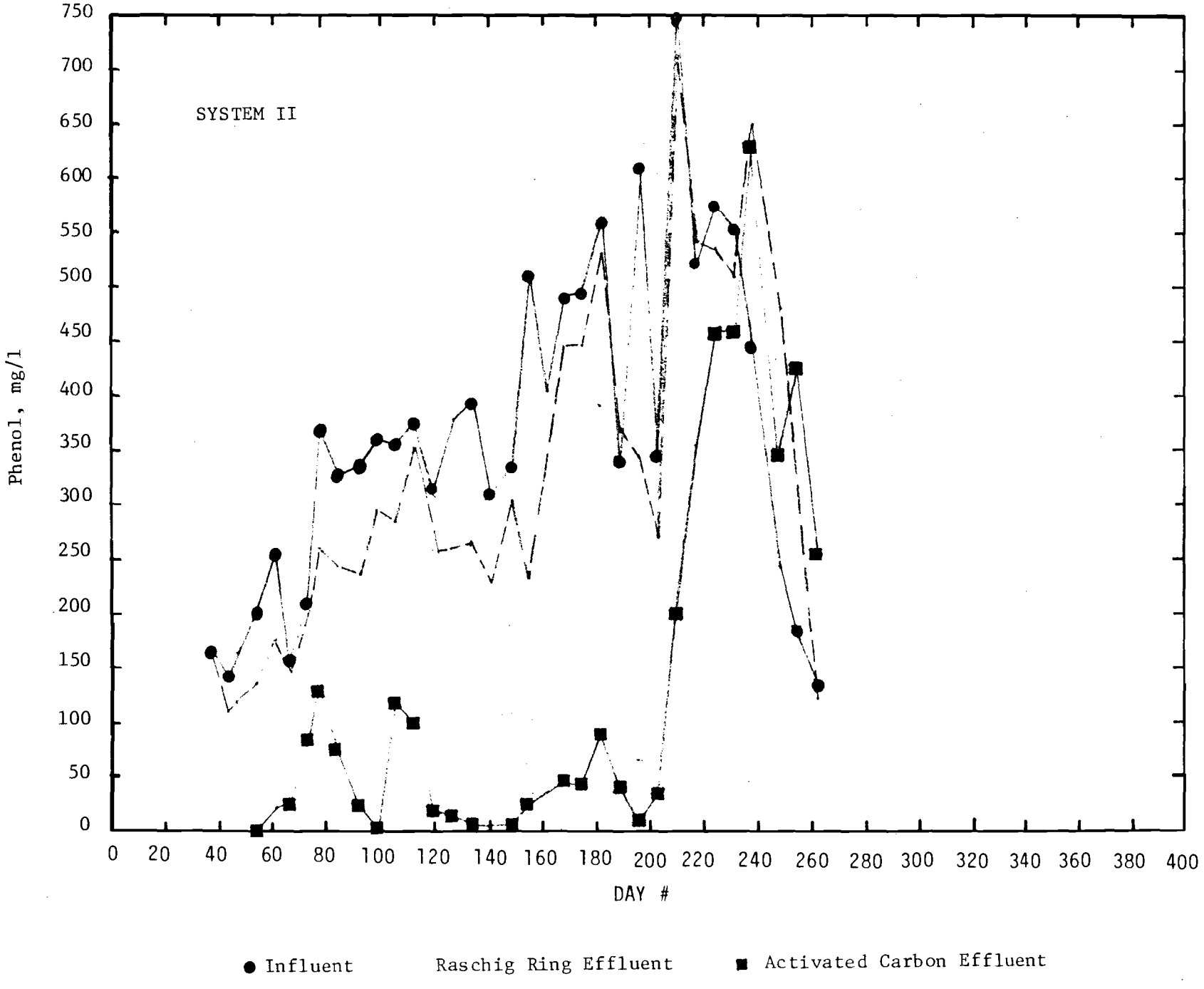

SYSTEM I
Phenol, mg/l
DAY #
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
Influent
Raschig Ring Effluent
Activated Carbon Effluent

Figure 7


SYSTEM II
Phenol, mg/l
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
Raschig Ring Effluent
■ Activated Carbon Effluent

Upon increasing the raw wastewater concentration to 15% the phenol concentration in the effluents slowly increased until it was equal to the influent concentration indicating a loss of biological activity in both systems.

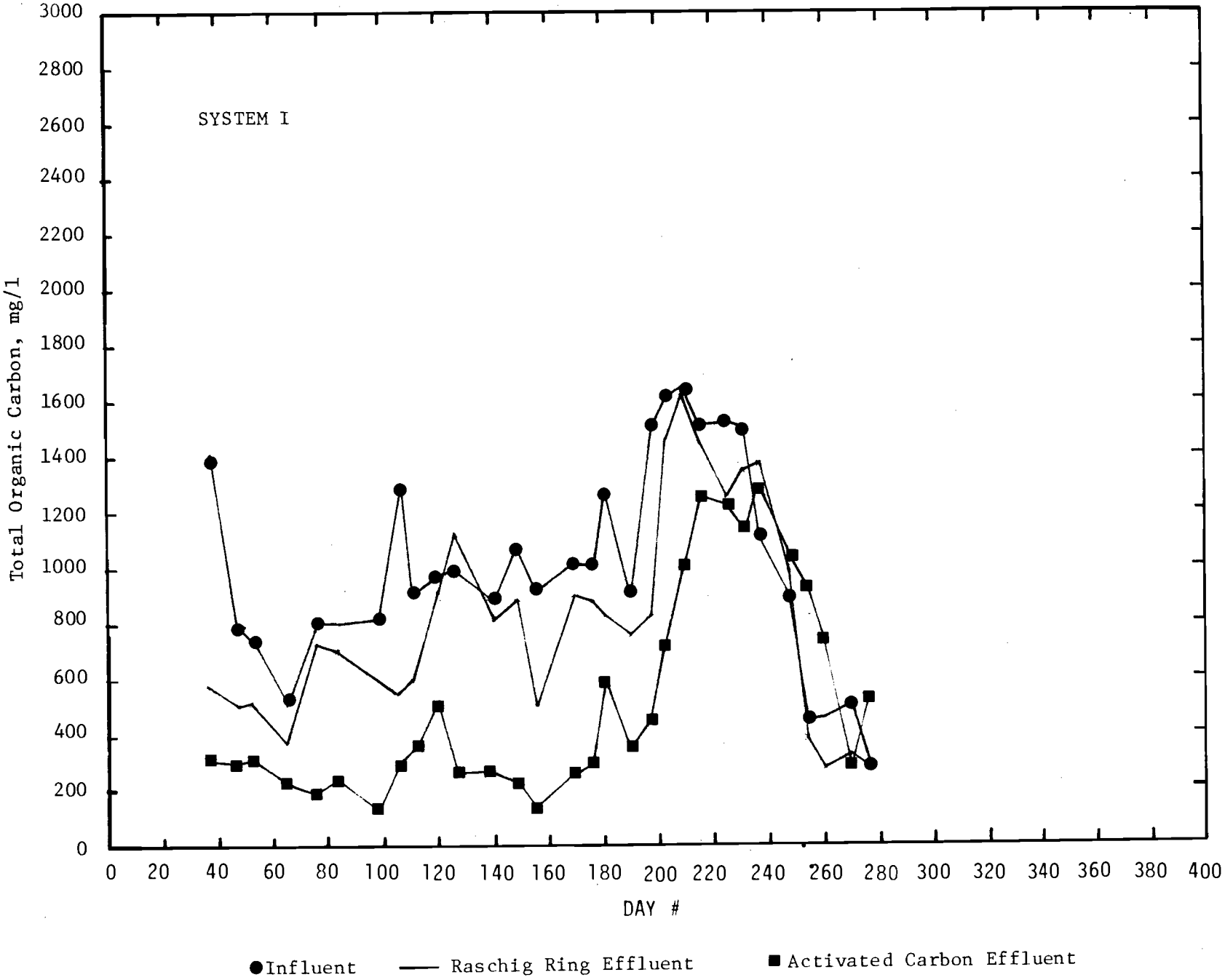
5. TOC and COD Removals

During the period day 147-195 the TOC and COD removal, Figures 9, 10, 11 and 12 averaged 67% and 76%, respectively for System I while those for System II were 72% to 81%, respectively. The range of TOC and COD removals have been from 57-88% and 60-83%, respectively for both systems with System II showing slightly better performance than System I.

Upon increasing the loading on day 196 effluent TOC and COD values for both systems slowly increased until the effluent values were equal to or greater than the influent values indicating less of biological activity and possibly the washout of lysis products from the dead bacteria.

6. pH, Alkalinity and ORP

The pH of the diluted wastewater ranged from 8.0 to 8.4 and decreased to 7.3 to 7.8 in the AC effluent until the systems failed at which time the pH in the effluent increased to a value of 8.0 to 8.3. ORP values also increased during the period of increased loading on the system indicating a loss of anaerobic activity. Alkalinity values increased as the wastewater concentration was increased.


SYSTEM I
Total Organic Carbon, mg/l
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
●Influent
—— Raschig Ring Effluent
■ Activated Carbon Effluent

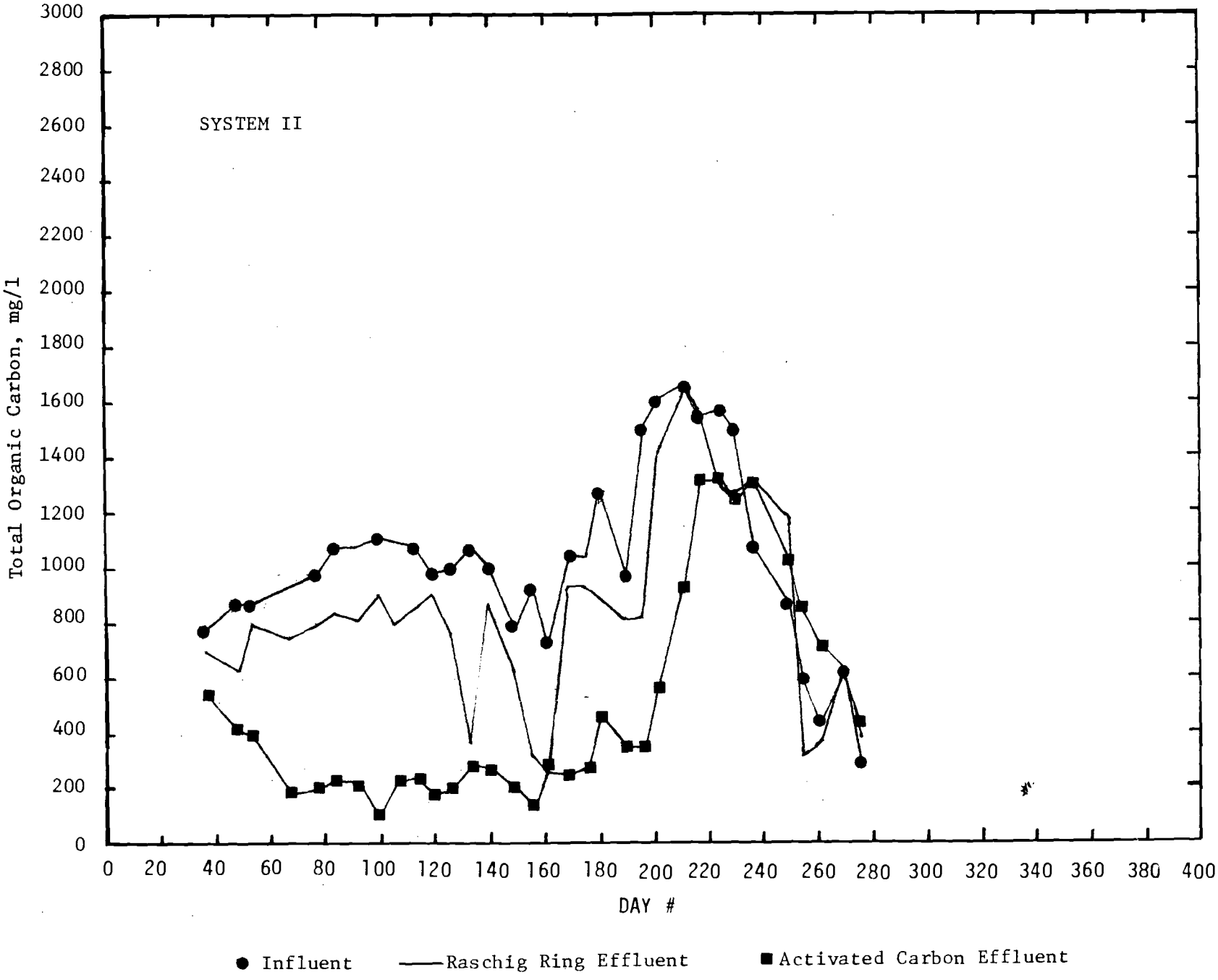
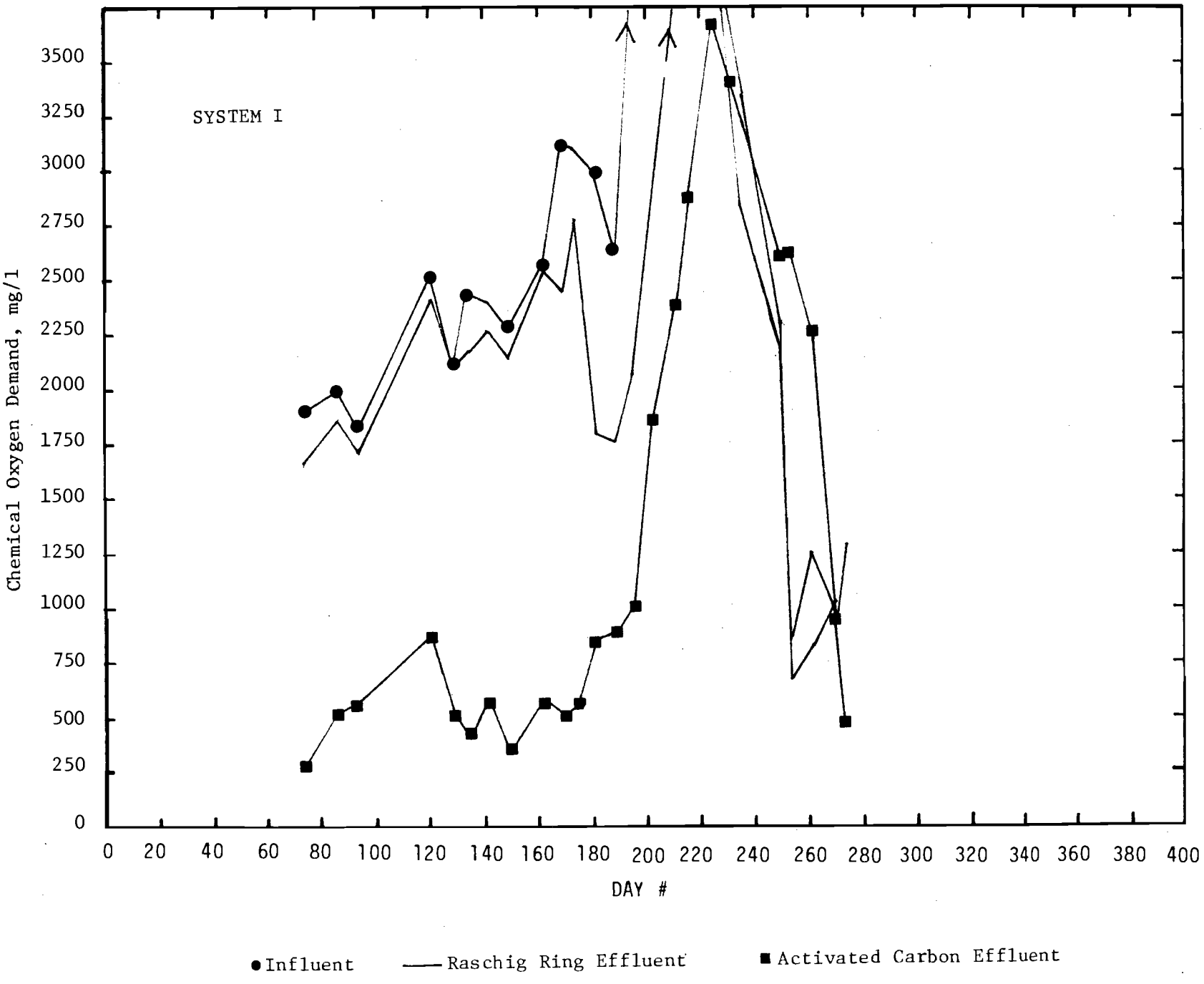

SYSTEM II
Total Organic Carbon, mg/l
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
——Raschig Ring Effluent
■ Activated Carbon Effluent

Figure 10


SYSTEM I
Chemical Oxygen Demand, mg/l
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
—— Raschig Ring Effluent
■ Activated Carbon Effluent

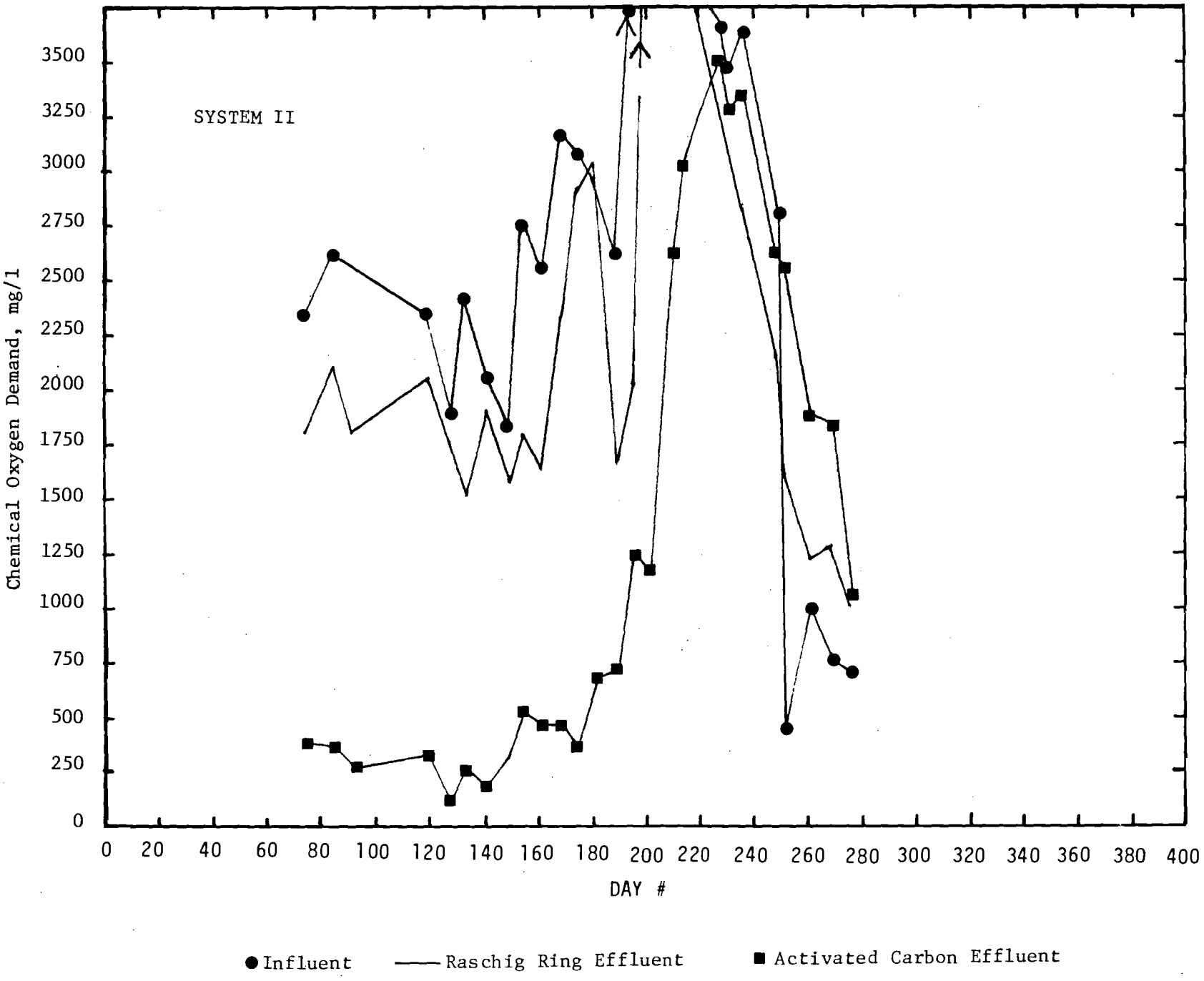

SYSTEM II
Chemical Oxygen Demand, mg/l
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
—— Raschig Ring Effluent
■ Activated Carbon Effluent

Figure 12

B. System III

1. Operation

System III has been acclimated to 10% raw wastewater according to the schedule in Table I. It has now been operated on a feed substrated of ~10% raw wastewater and phosphates for a period of 51 days. Data gathered during this psuedo steady state operation is presented in the following section.

2. Volatile Acid Production

Volatile acids concentration (Figure 13) have continued to decrease as the methanogenic population of organisms has become established. Final effluent concentrations are below 100 ppm.

3. Gas Production

Production of CH_4 and CO_2 have continued to increase (Figure 14) and reached a maximum production rate of 5.9 ℓ/day and an average value of 4.4 ℓ/day for the period day 138 through 194.

4. Phenol Removal

Phenol removal (Figure 15) have varied from 48 to 86% with an average removal of 69% for the steady state operating period. Effluent concentrations are approximately 100 ppm. These removal efficiencies for phenol are not as high as those were for Systems I and II. It is anticipated that the removal efficiencie will improve the longer the system is operated.

5. TOC and COD Removals

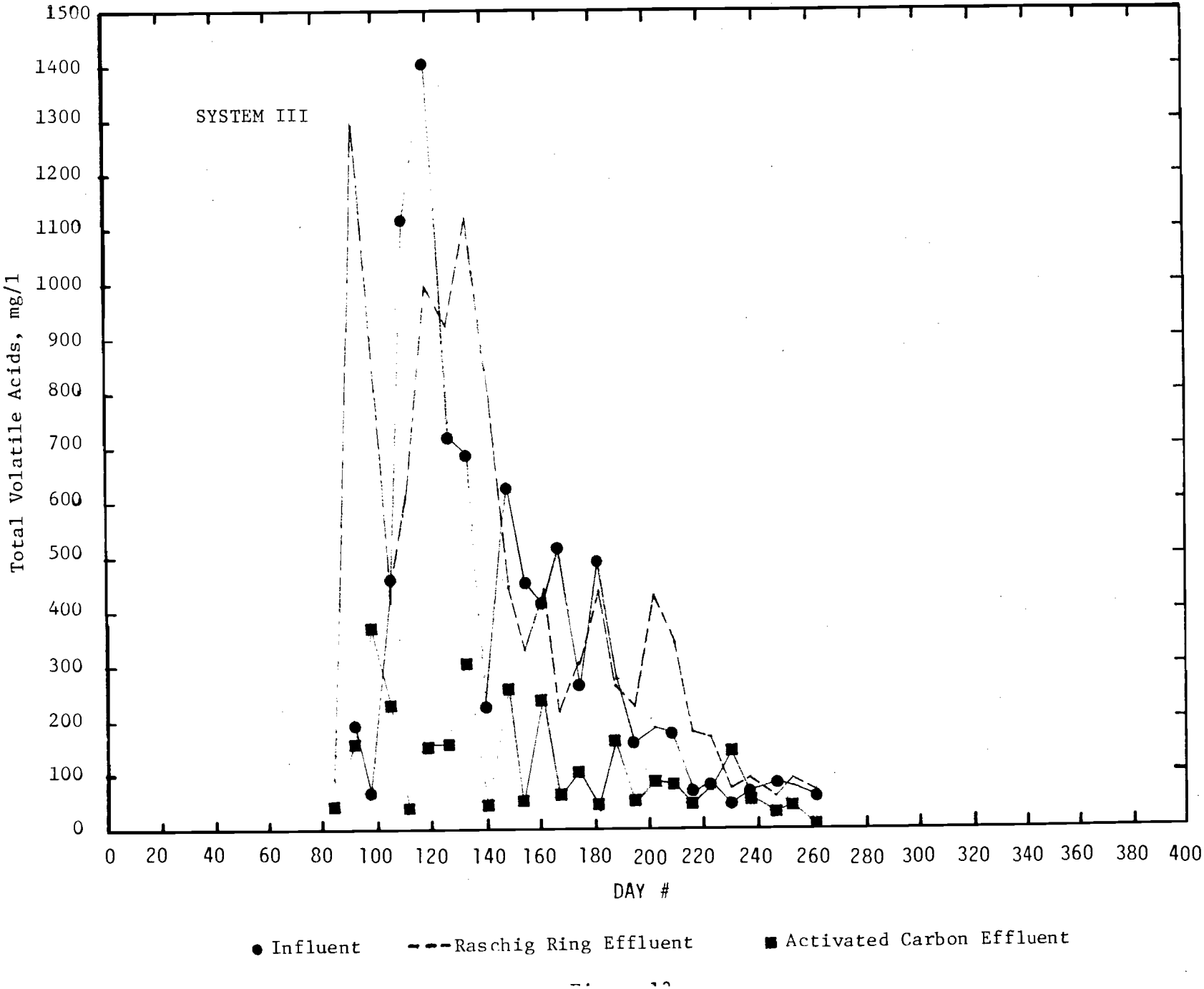
TOC and COD removals are still low compared to system I and II (Figure 16 and 17) averaging 54 and 62%, respectively.

6. pH, ORP and Alkalinity

Influent pH values have increased somewhat since the system began operating on only raw wastewater with a range from 7.4 to 8.4 with the final effluent fluctuating in pH from 7.4 to 8.1

TABLE I. FEED SOLUTION FOR SYSTEM III

Day of Operation	Feed Solution
97-131	Raw Wastewater (800 ppm TOC), Glucose (200 ppm TOC), Phosphates
132-139	Raw Wastewater (900 ppm TOC), Glucose (100 ppm TOC), Phosphates
140-present	Raw Wastewater (1000 ppm TOC), Phosphate


SYSTEM III
Total Volatile Acids, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
---Raschig Ring Effluent
■ Activated Carbon Effluent

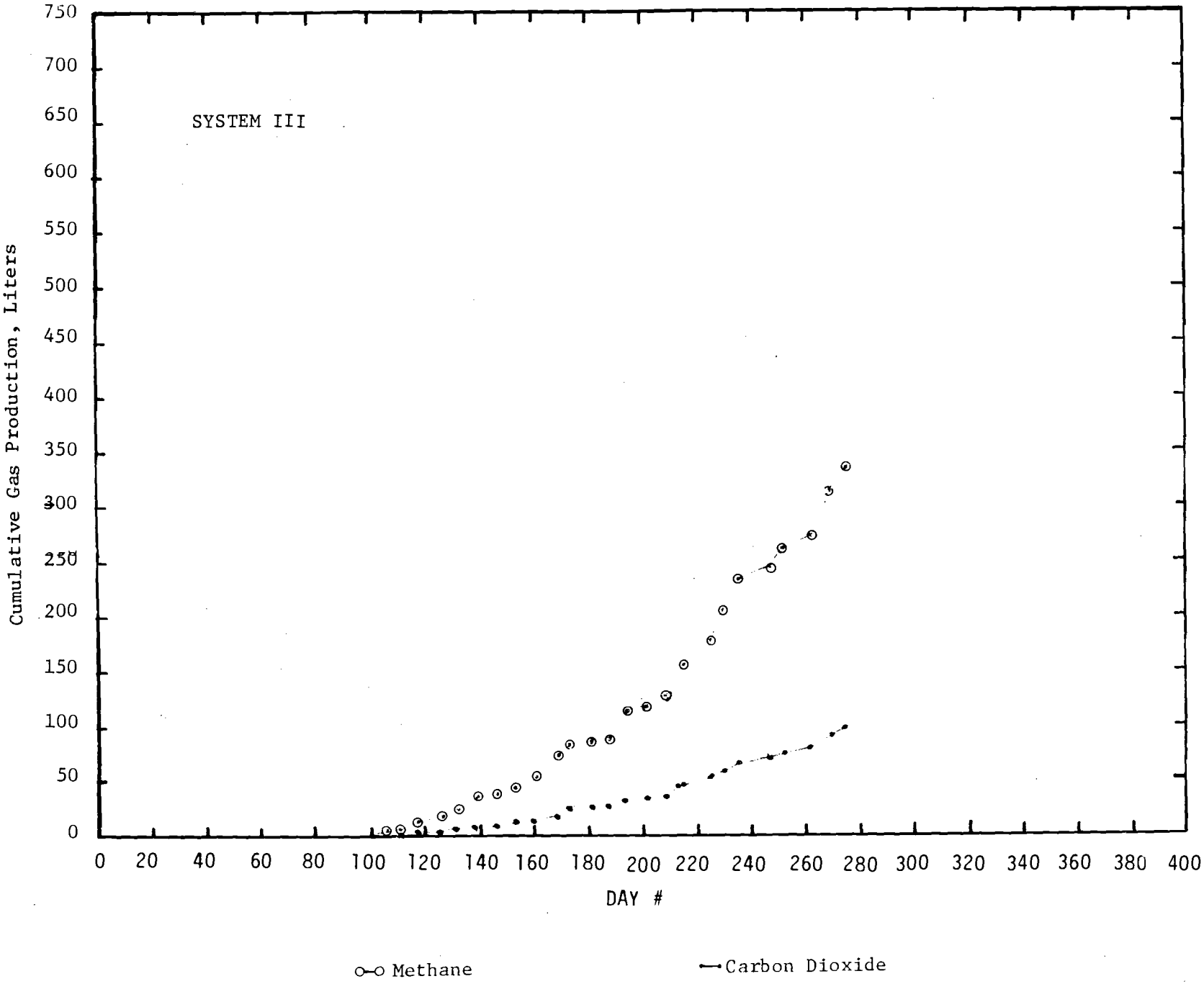
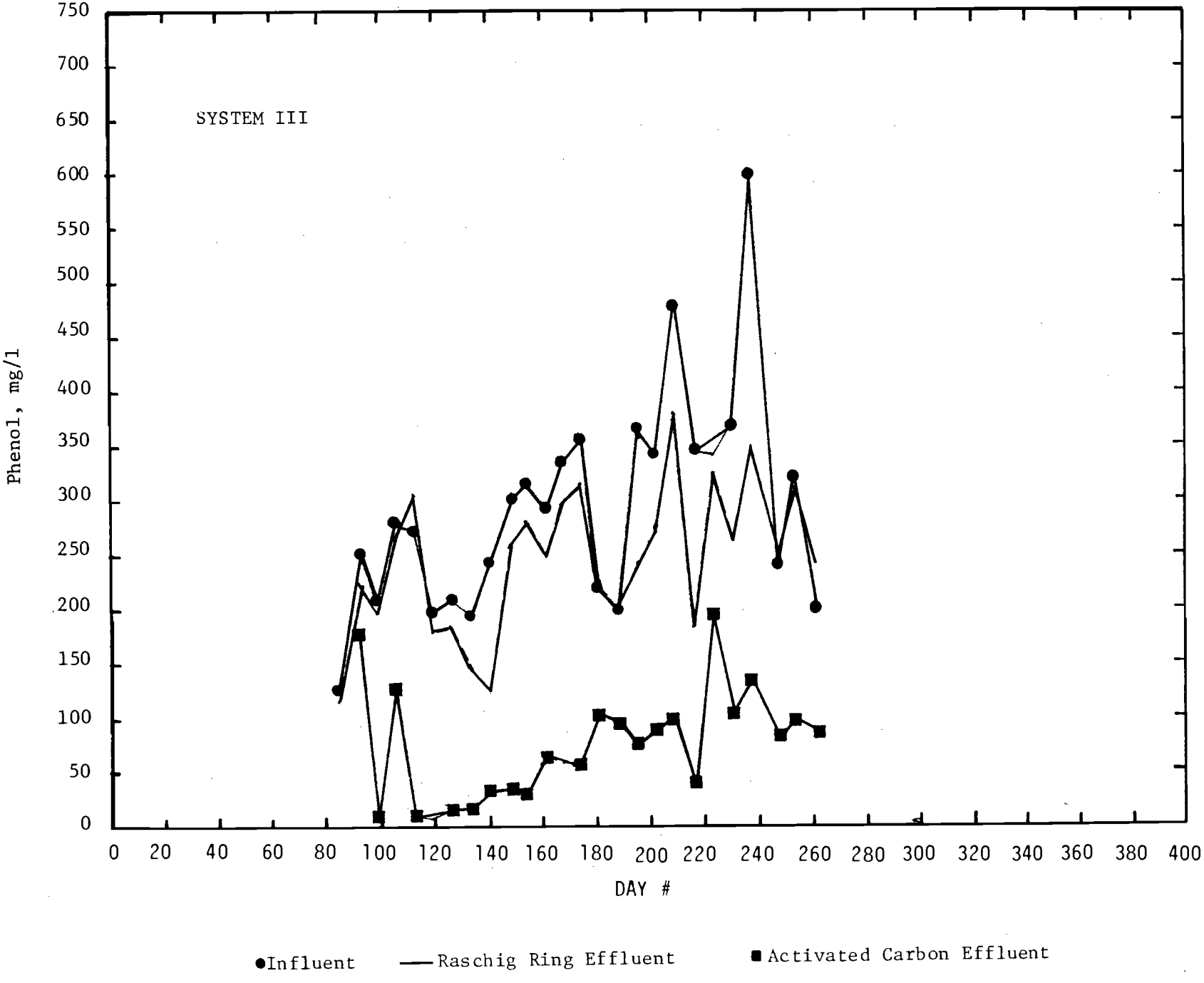

SYSTEM III
Cumulative Gas Production, Liters
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
Methane
Carbon Dioxide

Figure 14


SYSTEM III
Phenol, mg/l
DAY #
●Influent
—Raschig Ring Effluent
■Activated Carbon Effluent

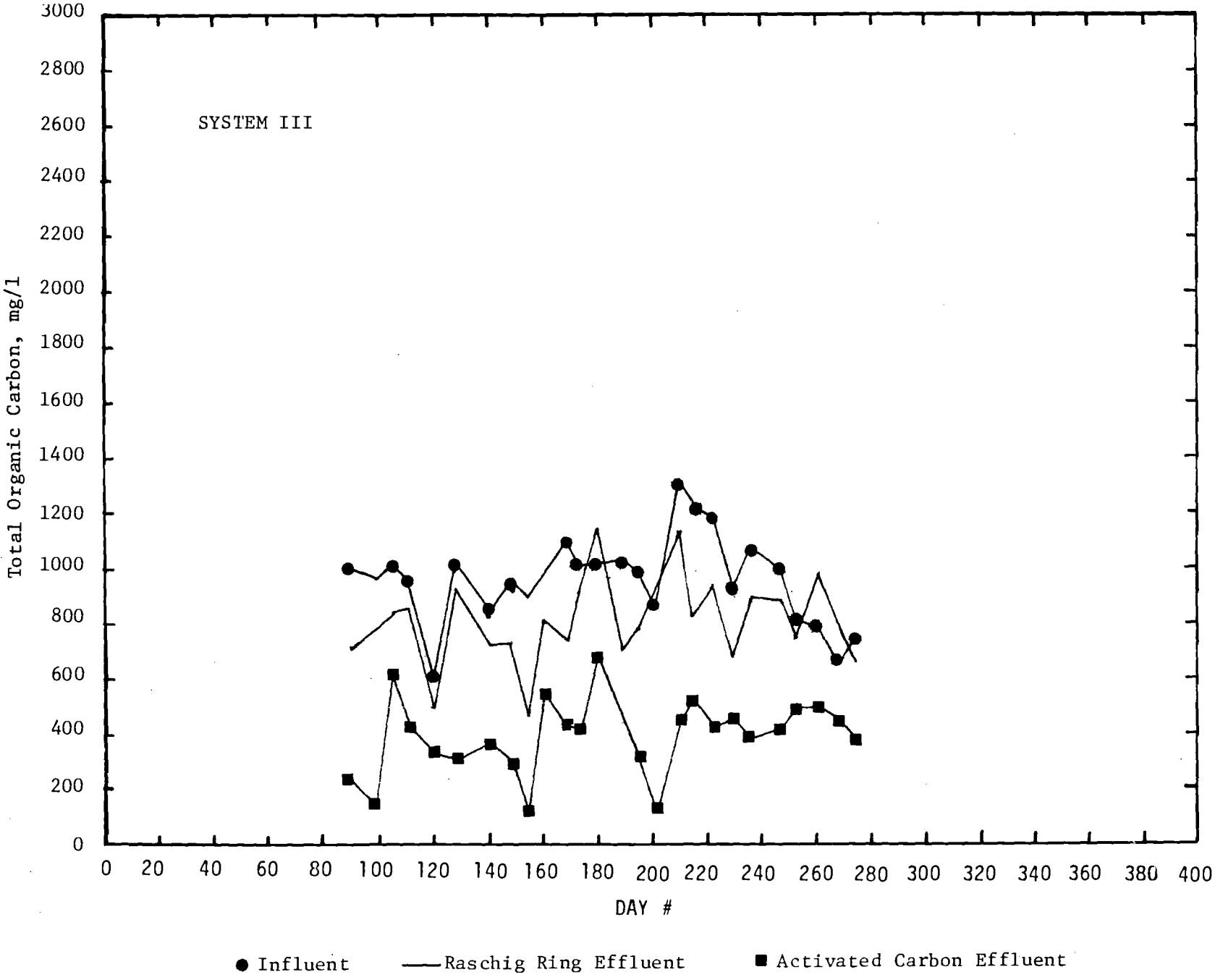
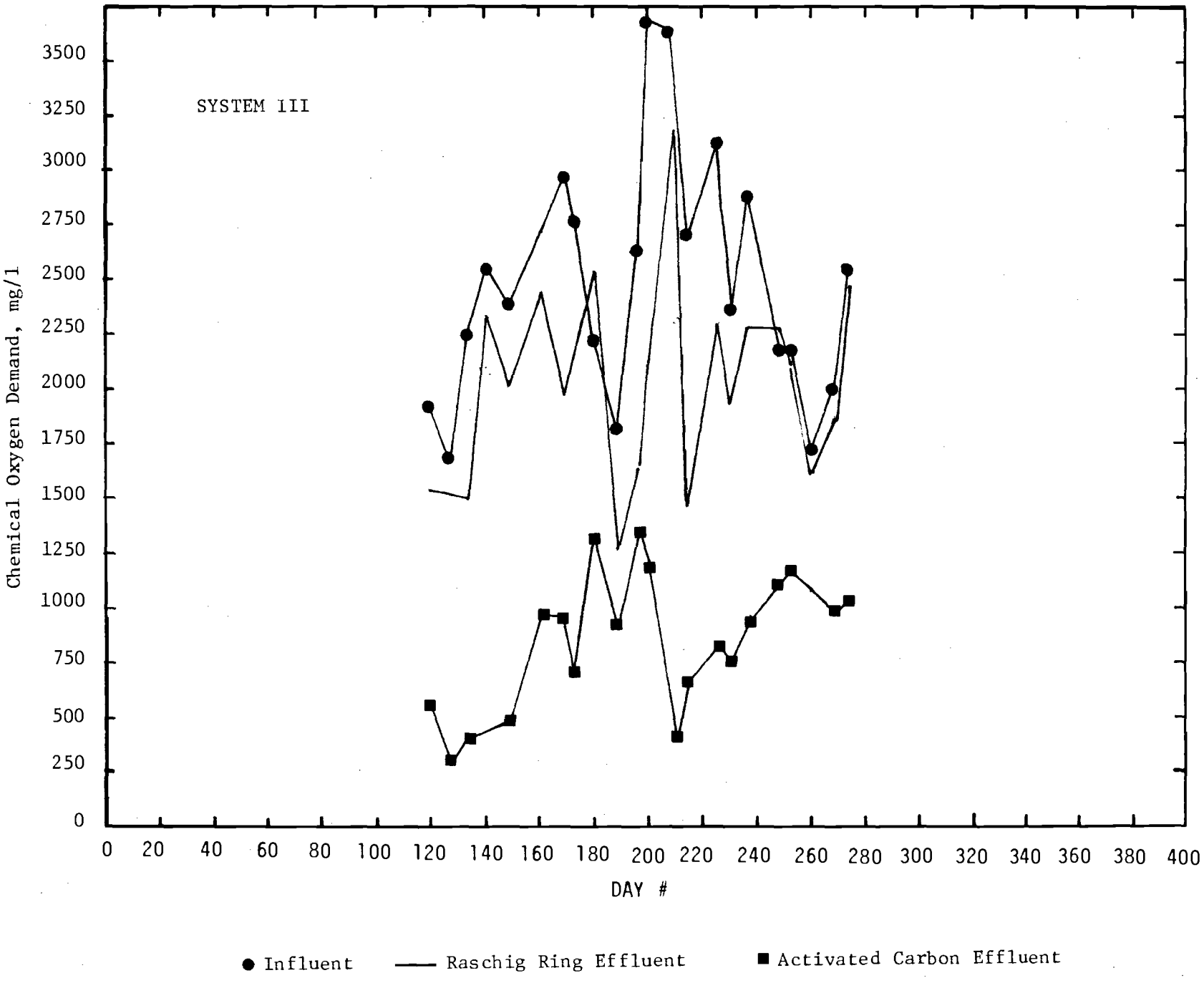

SYSTEM III
Total Organic Carbon, mg/l
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
——Raschig Ring Effluent
■ Activated Carbon Effluent

Figure 16


SYSTEM III
Chemical Oxygen Demand, mg/l
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
● Influent
—— Raschig Ring Effluent
■ Activated Carbon Effluent

Alkalinity increased slightly across the system with an average influent value of 1373 mg/l while the effluent has a value of 1478 mg/l.

ORP values continue to remain quite low in both columns with a range from -242 to -355 mv.

III. NITRIFICATION SYSTEM

1. Operation

The nitrification system has continued to be operated at a hydraulic residence time of 18 hours and a sludge age of approximately 22 days. The feed solution to the system has consisted of increasing concentrations of effluent from the anaerobic filters as indicated in Table II.

2. Results

The nitrification system has shown extremely good removals of not only NH_3 but also of residual TOC and COD in the wastewater.

NH_3-N, NO_2^--N, NO_3^--N influent and effluent concentrations are given in Table II for the five anaerobic effluent concentrations which have been treated. As can be see from data essentially complete nitrification has been occurring at all concentrations with conversion of the NH_3-N to NO_3^--N. However, it should be noted that the level of NO_2^--N has started to increase in Phase 2 indicating a possible inhibition in the conversion of NO_2^--N to NO_3^--N at this concentration of wastewater. Figures 18, 19 and 20 are plots of the data for the N containing species. Figures 21 and 22 give the influent - effluent values of TOC and COD for the systems. Current removal efficiencies for the above species are 80%, 77% and 99% for TOC, COD and NH_3-N, respectively.

TABLE II. OPERATION PARAMETERS AND REMOVAL RATES FOR NITRIFICATION SYSTEM

Parameters	Phase 1-a		Phase 1-b		Phase 1-c		Phase 1-d		Phase 2(up to 7/1)	
Dilution ratio	1:9		1:3		1:1		3:1		No dilution	
NH_c-N loading ($kgNH_3$-N/kgMLSS/d)	0.054		0.076		0.129		0.125		0.154	
COD loading (kgCOD/kgMLSS/d)	0.083		0.125		0.126		0.194		0.277	
MLSS (mg/l)	1560		1900		2655		3393		3130	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
NH_3-N (mg/l)	65	0.7	111	0.4	269	1.8	425	1.6	482	5.0
NO_3^--N (mg/l)	0.5	57	0.3	101	0.8	221	2.1	354	3.1	402
NO_2^--N (mg/l)	ND*	ND	0.02	0.3	0.02	0.2	ND	0.3	ND	30.8
TOC (mg/l)	50	30	111	30	227	46	466	56	640	132
COD (mg/l)	100	51	182	48	263	91	659	91	867	192
Alkalinity (mg/l)	425	50	975	310	1868	313	2798	386	3430	745
pH	7.8	6.9	8.0	7.9	8.0	7.6	8.1	7.7	8.2	8.0

*ND = Not determined
SRT = 22 days
HRT = 18 hrs

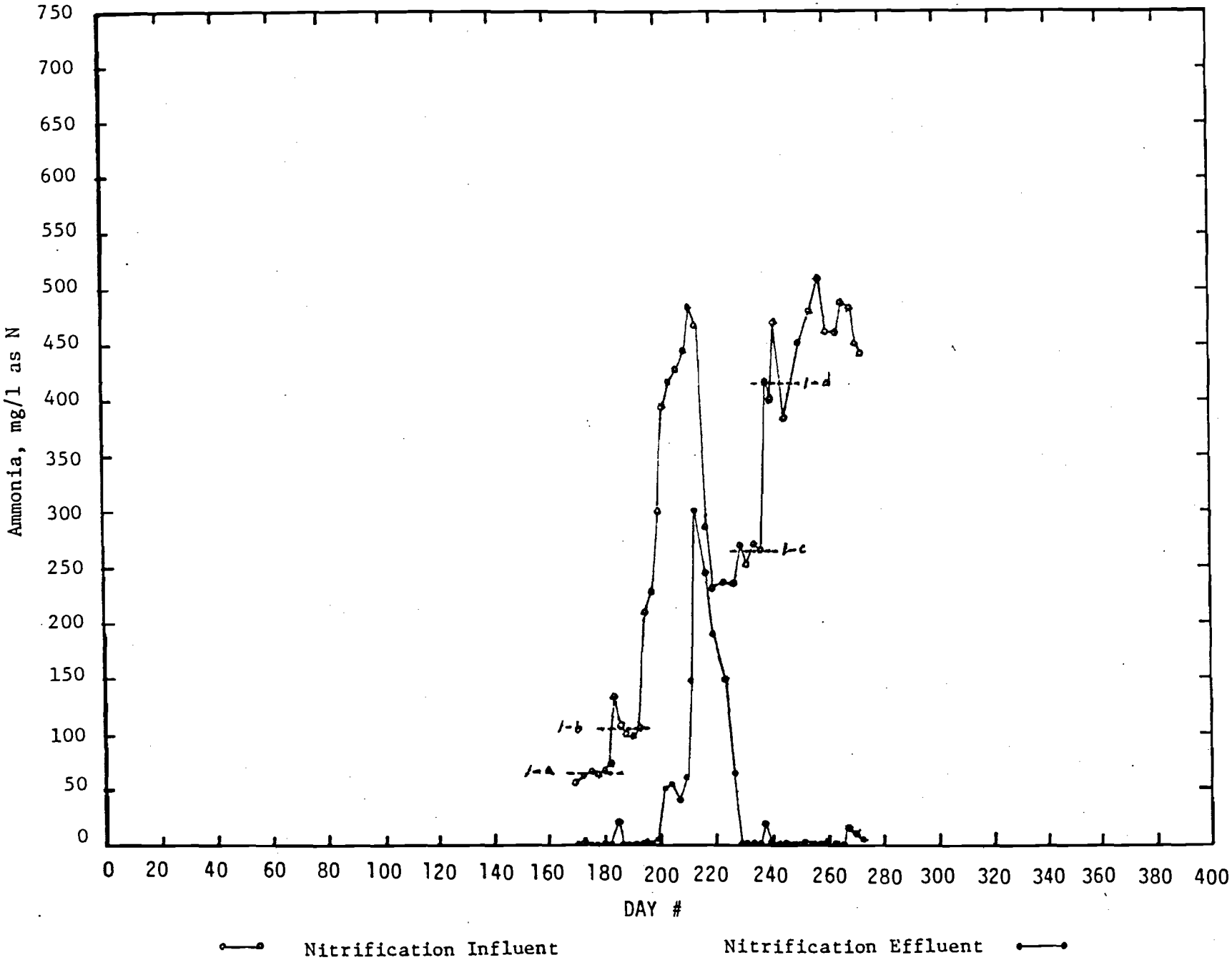

Ammonia, mg/l as N
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
I-a
I-b
I-c
I-d
Nitrification Influent
Nitrification Effluent

Figure 18

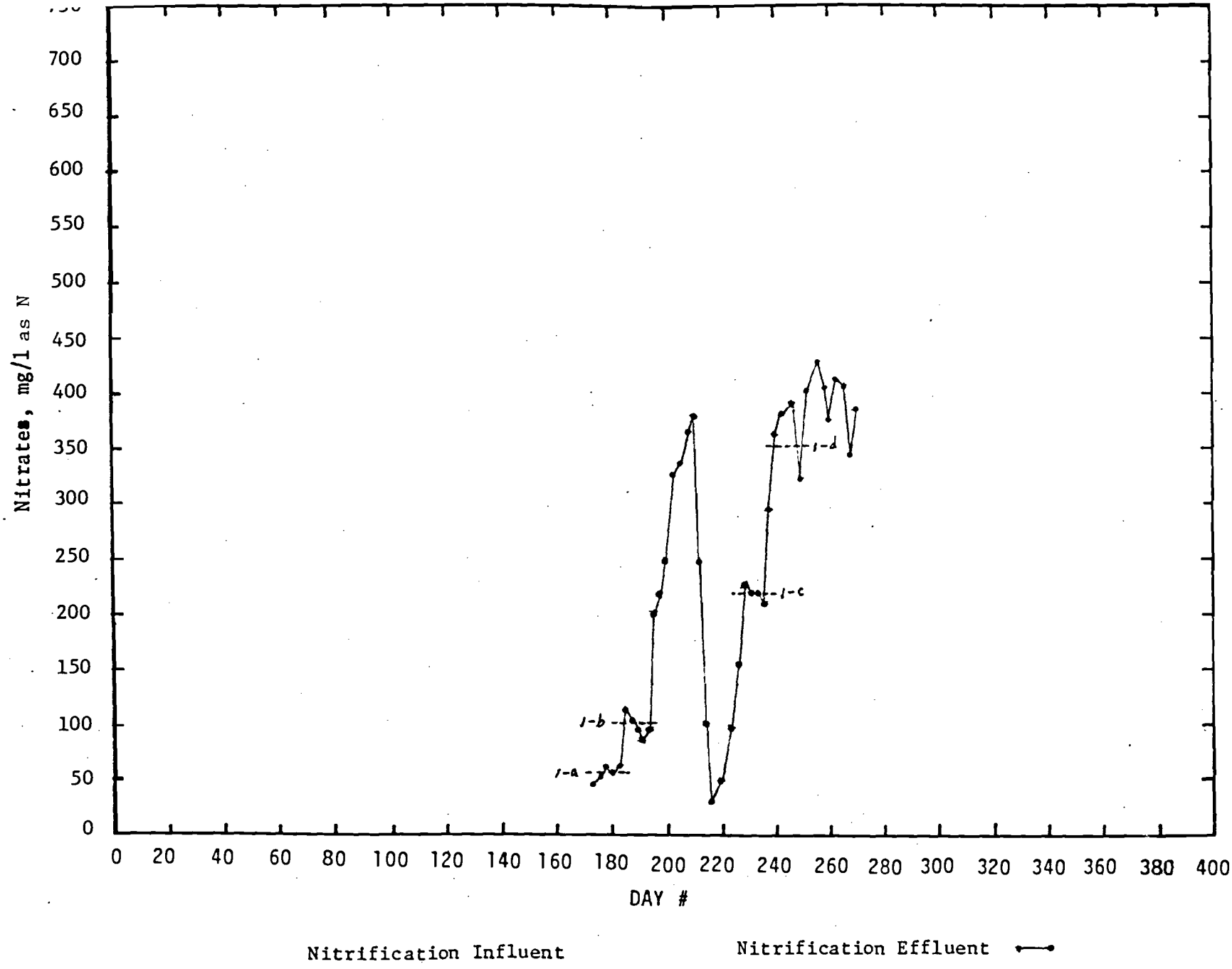
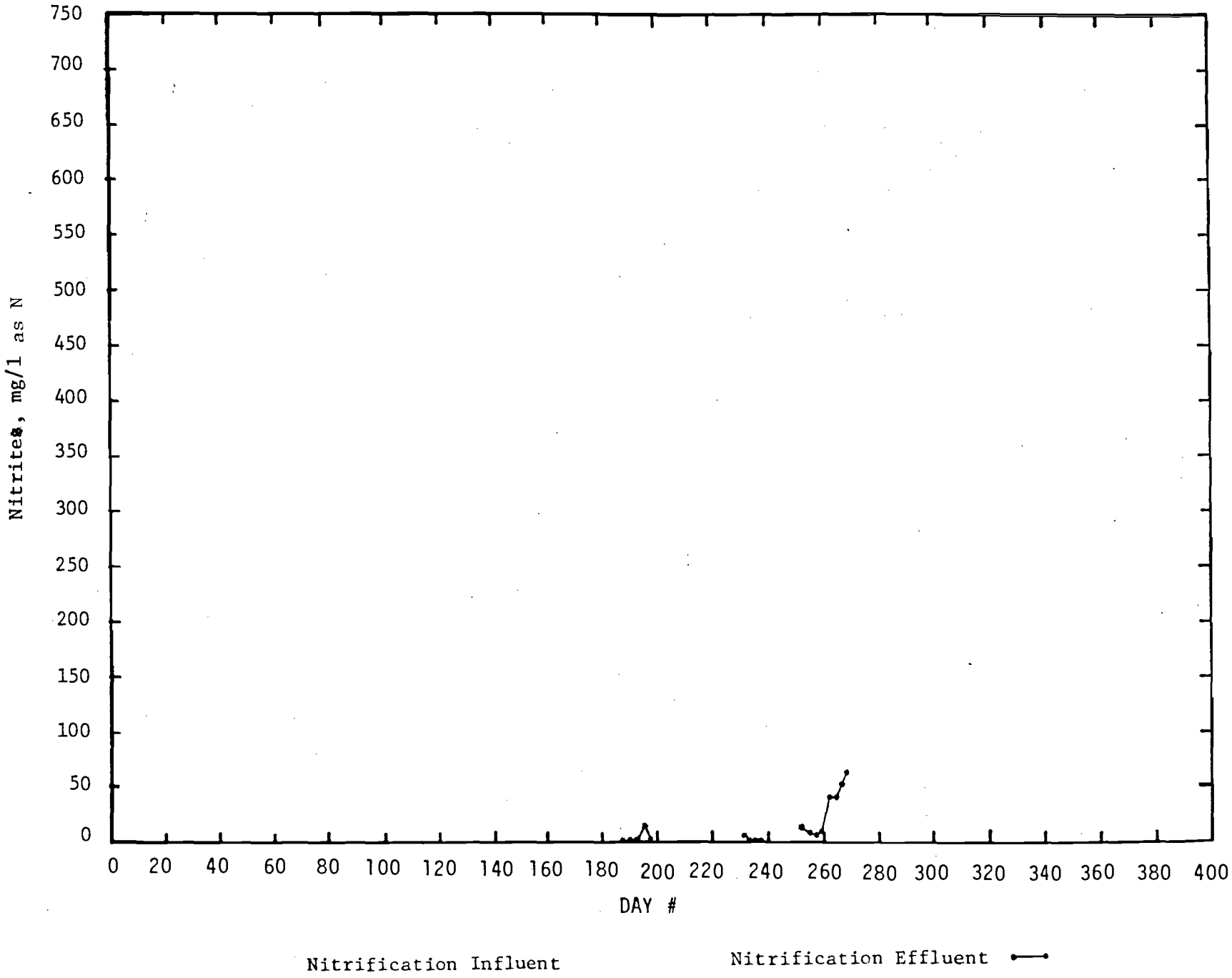

Nitrates, mg/l as N
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
1-a
1-b
1-c
1-d
Nitrification Influent
Nitrification Effluent

Figure 19


Nitrites, mg/l as N
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
Nitrification Influent
Nitrification Effluent

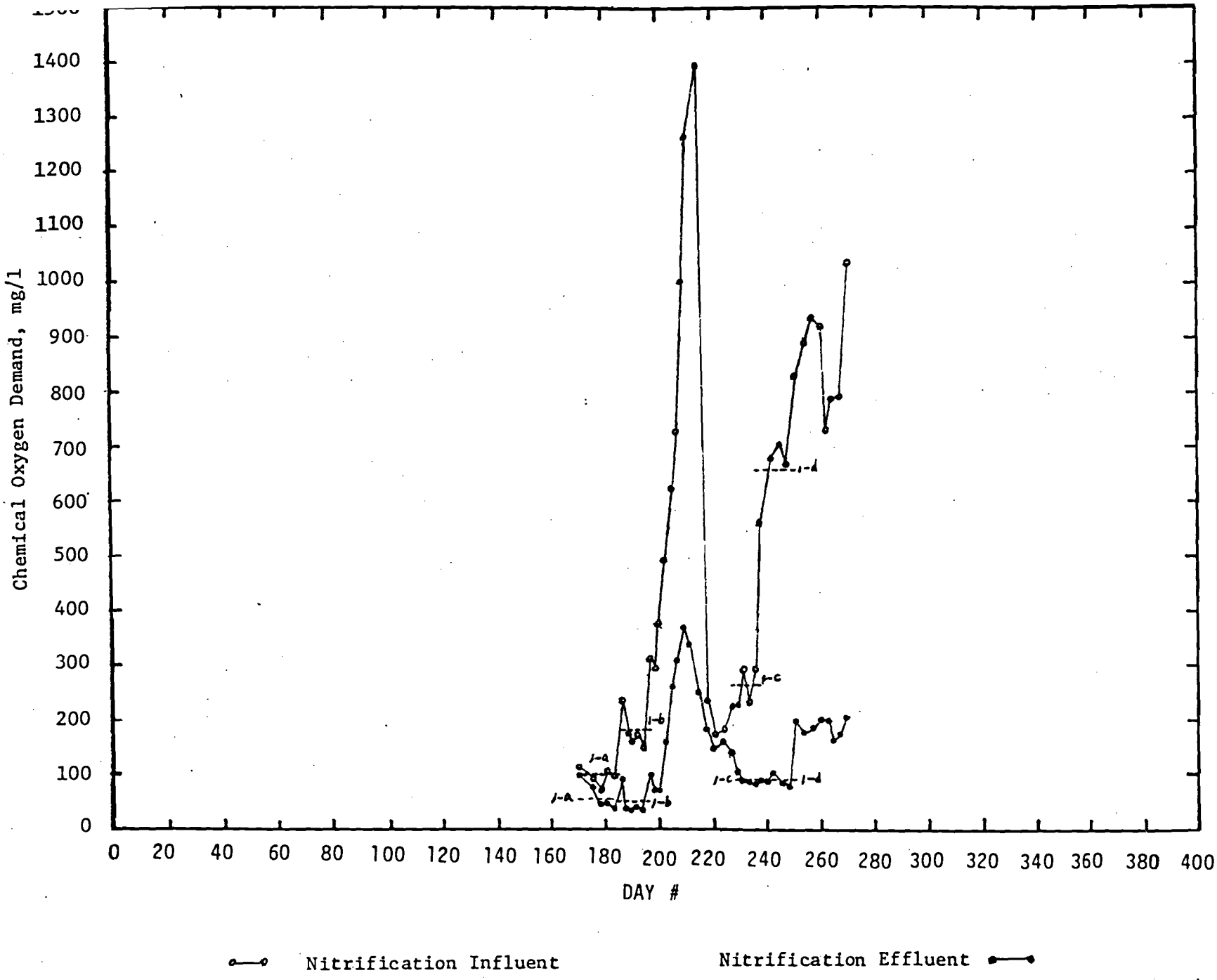

Chemical Oxygen Demand, mg/l
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
I-A
I-B
I-C
I-D
Nitrification Influent
Nitrification Effluent

Figure 21

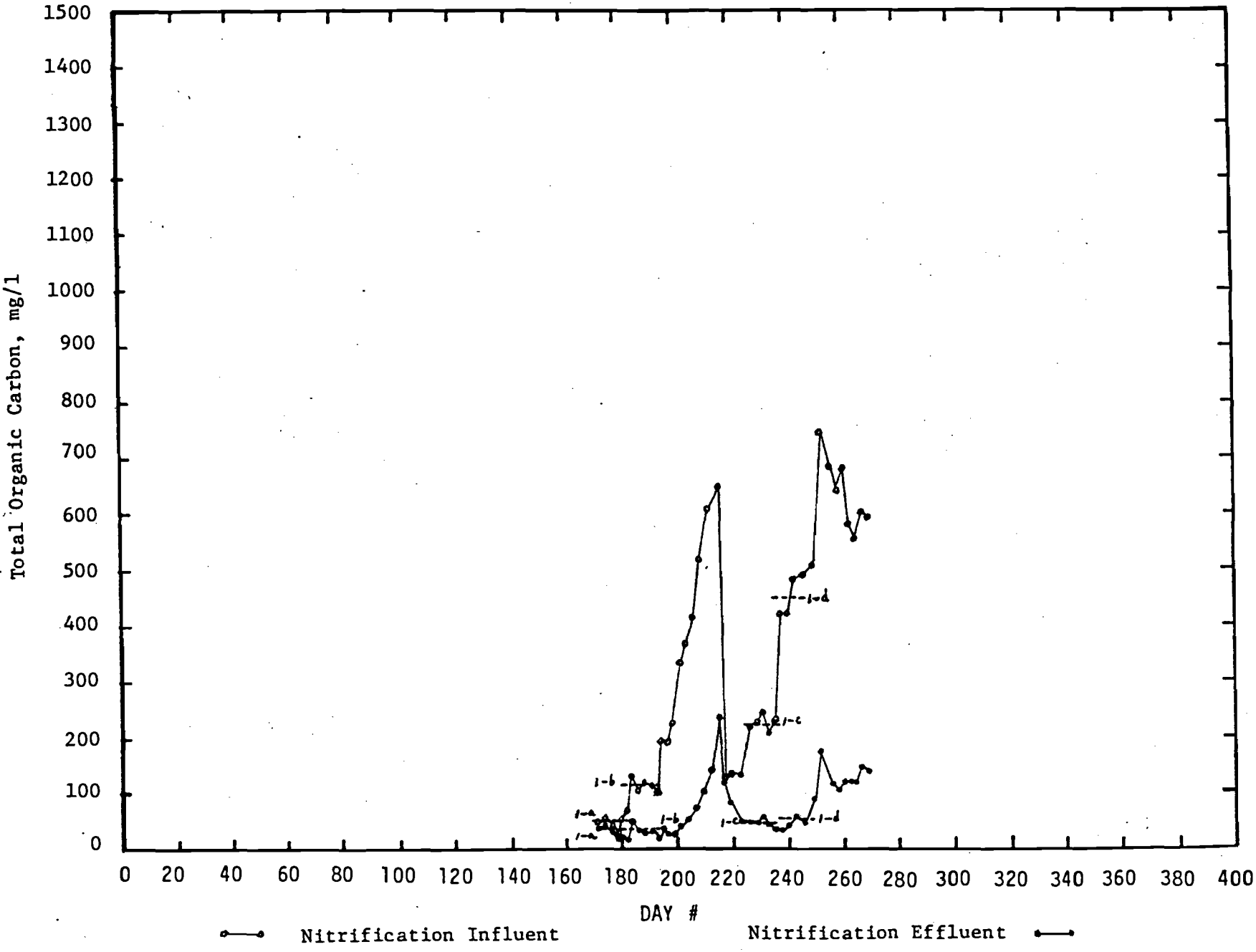

Total Organic Carbon, mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400
DAY #
Nitrification Influent
Nitrification Effluent
1-a
1-b
1-c
1-d

Figure 22

IV. SOLVENT EXTRACTION SYSTEM

1. System Operation

Difficulties have been encountered in efficient operation of the continuous extraction system. The pore size (~50μm) in the stainless steel frits is such that only wastewater samples containing relatively large amounts of tar are efficiently mixed in the system and give good extraction results. Clean wastewater samples allow the MIBK to pass easily through the frits with very little mixing. The current frits are being replaced with stainless steel frits of small pore size (~10μm) to alleviate the mixing problems with all wastewater samples.

V. AMMONIA STRIPPING SYSTEM

1. Ammonia Stripper Operation

Preliminary operation of the air stripping tower gave low removal efficiencies (~10%) due to short circuiting of the wastewater along the walls of the column. Liquid redistribution plates are being installed in the column in order to prevent this short circuiting from occurring.

VI. FUTURE WORK

Steady state operating parameters are being collected for System III while Systems I and II are being reacclimated. As soon as Systems I and II show sufficient operational viability the loading on System III will be increased slightly (~20%) and the hydraulic retention time decreased (~20%) to maintain a constant loading in System III at a higher wastewater concentration. System III will then be allowed to reach steady state and operational efficiencies will be reevaluated.

Increased loading to the nitrification system will be evaluated to determine the maximum loading rate the system can sustain.

Solvent extraction and air stripping studies will be continued in order to produce a pretreated wastewater for anaerobic treatment. In addition investigation will continue in order to identify the specie or species causing inhibition of the anaerobic system at 15% wastewater concentration.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #5
September 1982

by

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Project Officer

Dr. Leland Paulson

TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from July 1, 1982 through September 30, 1982 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. CE-AC18-81FC10297). The major efforts have been directed toward reacclimation of two of the anaerobic treatment systems, continued steady state operation of the third system at an ~10% raw wastewater loading and operation of a nitrification system on full strength effluent from the third anaerobic treatment system. The progress of these efforts are depicted in the Gant Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.

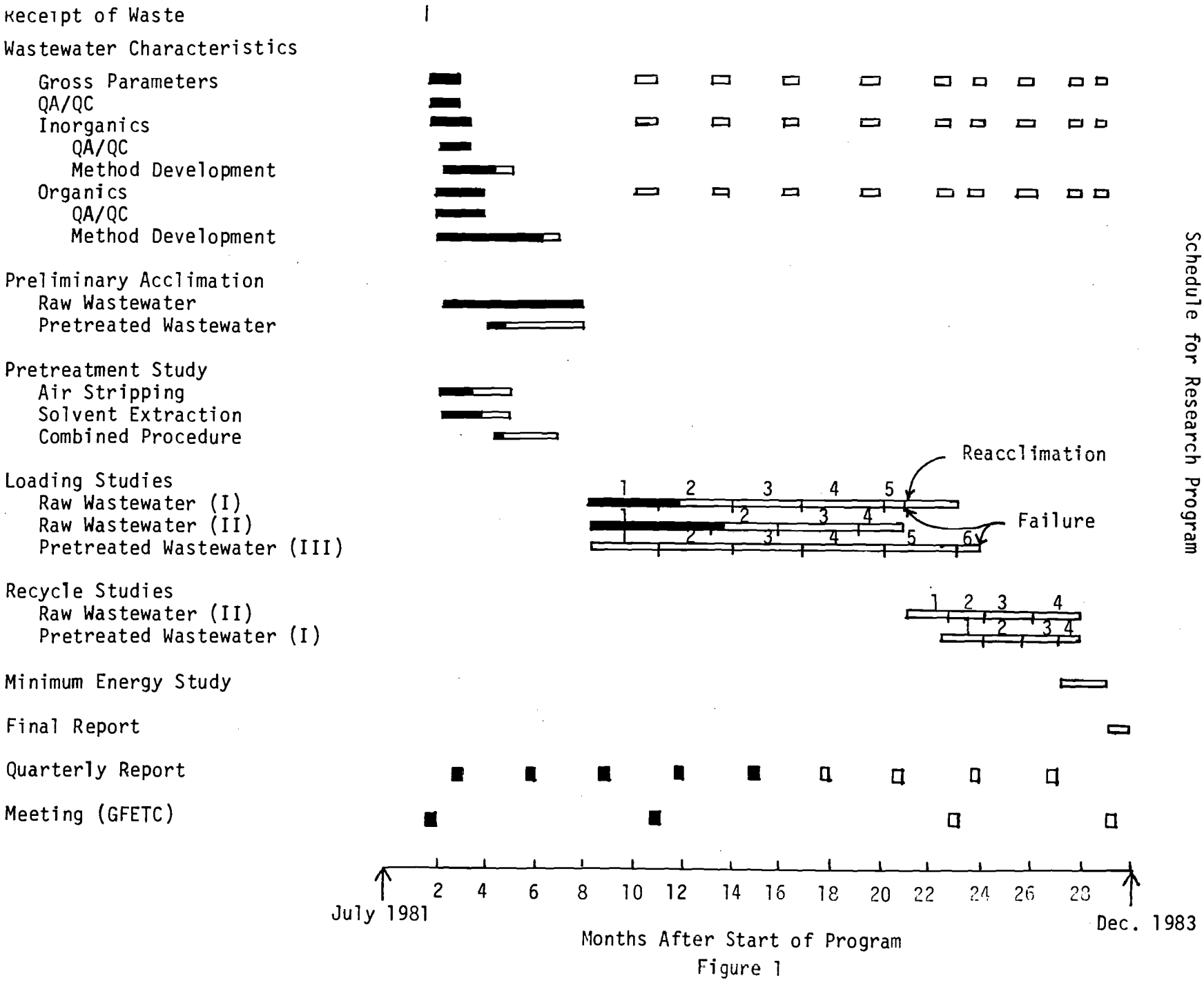
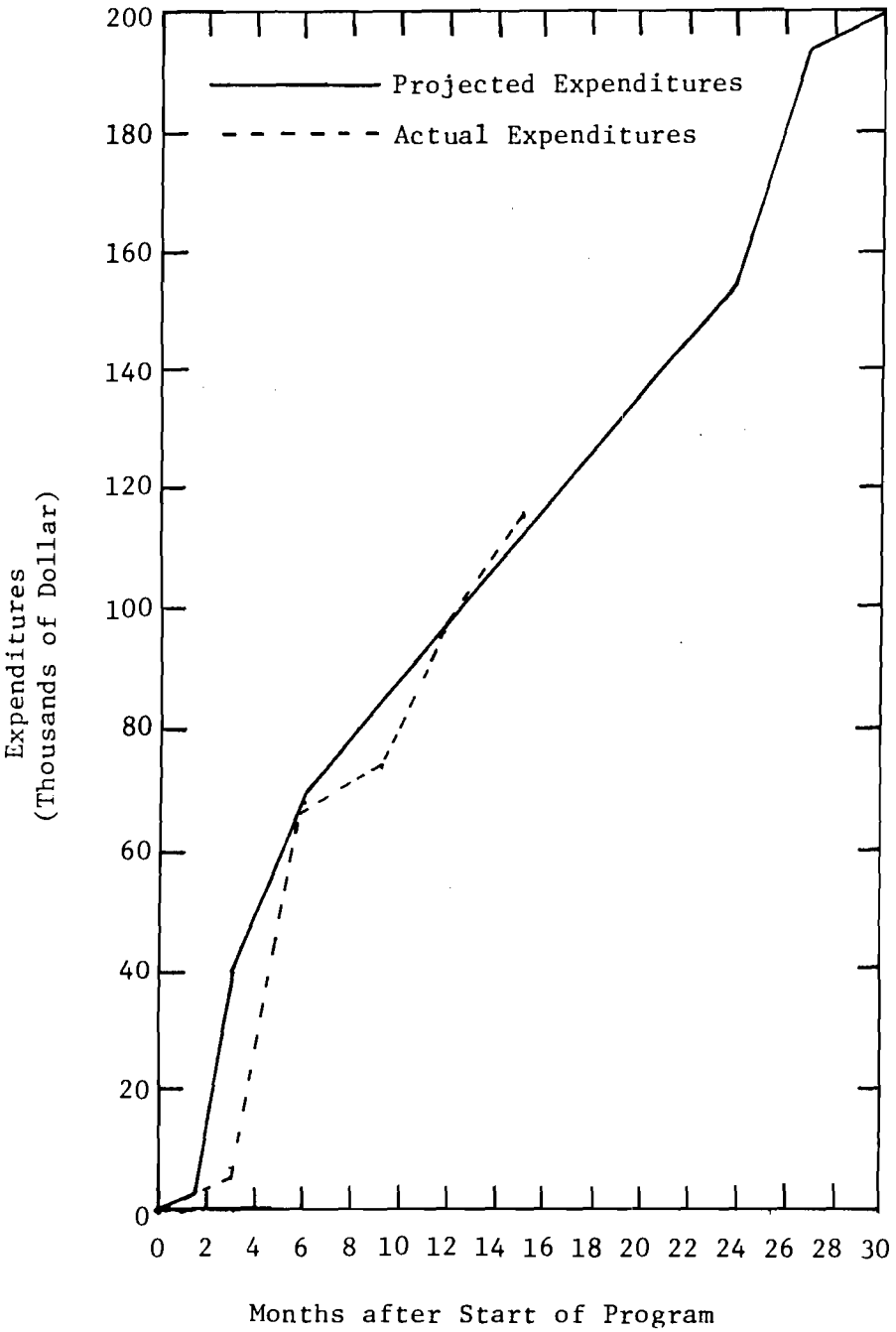

TASK
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
Method Development
Preliminary Acclimation
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
July 1981
Dec. 1983
Months After Start of Program
Schedule for Research Program

Figure 1



Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

Figure 3

II. ANAEROBIC TREATMENT SYSTEMS

A. System I and II

1. Operation and Loading Changes

System I and II were reseeded on day 254 with sludge from a municipal anaerobic sludge digester and feed substrate consisting of the following was initiated:

System I: 500 ppm raw wastewater TOC at 5 ml/min

System II: 600 ppm raw wastewater TOC and 100 ppm glucose TOC at 5 ml/min.

The Systems were allowed to operate for 36 days (day 289). During this period minimum TOC, COD and phenol removals were observed and in some instances effluent values were greater than influent values. Only small amounts of gas were produced, 0.10 l/day for System I and 0.75 l/day from System II. Therefore, on day 290 the treated effluent from System III was used to supplement the feed to the activated carbon columns in Systems I and II. System I and II were then operated for an additional 60 days (day 350). During this time period TOC and COD removals remained low, 10.2% and 20.8% for TOC and 32.8% and 21.2% for COD for System I and II, respectively. Phenol removals were negative averaging -27.5% and -4.9% for Systems I and II, respectively.

Gas production remained very low, 0.34 l/day for System I and 0.42 l/day for System II.

The above data was interpreted as follows. The low TOC and COD removals and low gas production indicate an extremely inhibited biological system with very little bioactivity. The negative pehnol removals indicate apparent saturation of the activated carbon with the resulting desorption of phenol by more strongly adsorbing species present in the influent.

Therefore, to alleviate the apparent toxicity and/or inhibition and to replace the exhausted activated carbon the following steps will be undertaken:

1) Systems I and II will be redesigned into the following Systems:

a) System IV which will consist of three (3) activated carbon columns in series with the activated carbon column from System I as the first column and two (2) columns loaded with fresh activated carbon column subsequent to the first column. The system will be operated as before with the activity in each carbon column being closely monitored. As activity in the first column becomes retarded or ceases the column will be removed from service, the carbon replaced and the column placed back into service as the last column in the series of three.

b) System V will consist of a single activated carbon column with provision for removing and adding activated carbon on a routine basis. From data collected on System I, II and III an initial estimate of carbon exhaustion will be made and a schedule set up to periodically replace a fraction of the activated carbon in System V with fresh activated carbon.

The already exhausted carbon from System I and II is currently being analyzed for the major adsorbed constituents. Initial data indicates that the major adsorbed species are the cresols and phenol with the cresols being preferentially adsorbed in much hgih quantities than phenol or other species. Carbon from System III and from Systems IV and V when they are operating will also be analyzed for major adsorbed species.

Methods for regeneration of the exhausted carbons will also be suggested and possible work in this area will be proposed.

B. System III

1. Operation

System III has now been operated for an additional 90 days on ~10% raw wastewater at a flow rate of 10 ml/min.

System efficiency has remained fairly good with average removal for the 90 days being 42.0%, 44.4% and 60.9% for TOC, COD and phenol, respectively. Gas production has remained relatively high with an average production of 6.6 l/day and a methane content of 77.2%. However, close examination of the data indicates a very slight but steady decrease in performance based on phenol removal, both overall and especially in the activated carbon column.

Therefore, it is proposed to monitor System III very closely, especially for phenol and cresols and begin a program of periodic carbon replacement if the analysis indicates a continued decrease in System III performance and exhaustion of the activated carbon therein.

III. Nitrification System

1. Operation

The nitrification system has been operated on a feed solution consisting of undiluted effluent from Anaerobic System III supplemented with $NaHCO_3$ to provide additional alkalinity for the conversion of NH_3-N to NO_3^--N. The system was operated under two different loading conditions as shown in Table 1.

Removal of residual TOC, COD, TKN and NH_3-N were all excellent as shown in Table II. The system is still being operated in order to furnish a nitrified waste for a planned denitrification system to be put in operation in the near future.

Table 1. Operational Parameter - Nitrification System

Stage	Duration	SRT, days	HRT, hours	NH_3-N Loading*	COD Loading*
1	38 days	22	18	0.26	0.49
2	45 days	31	30	0.15	0.35

*Kg/KG MLVSS/day

Table II. Nitrification System Influent and Effluent Parameter

Stage	Parameter	Influent, mg/l	Effluent, mg/l	% Removal
1	TOC	622	127	80
2	TOC	776	72	91
1	TKN	-	-	-
2	TKN	601	18	97
1	NH_3-N	477	17	96
2	NH_3-N	527	4	99
1	COD	894	206	77
2	COD	1286	189	85
1	NO_3^--N	-	383	-
2	NO_3^--N	-	485	-
1	NO_2^--N	-	48	-
2	NO_2^--N	-	16	-

IV. and V. SOLVENT EXTRACTION AND AMMONIA STRIPPING

Due to the difficulty encountered in reacclimating Anaerobic System I and II and the apparent slow degradation of performance in Anaerobic System III further work on both solvent extraction and ammonia stripping has been delayed until the actual cause and possible remedies for the apparent inhibition/toxicity problem have been elucidated. When that problem has been solved the desirability and/or necessity and degree of solvent extraction and ammonia stripping will be reevaluated and the work continued.

VI. FUTURE WORK

Immediate future work has been outlined in each previous section. In addition a denitrification system will be constructed and operated using the effluent from the nitrification system in conjunction with methanol for NO_3^--N removal.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #6
December 1982

by

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TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from October 1, 1982 through December 31, 1982 on the DOE research program on "Anerobic Treatment of Gasifier Effluents" (Contract No. OE-AC18-81FC10297). The major efforts have been directed towards: 1) the operation of two anaerobic systems treating ≈10% strength raw wastewater, 2) The operation of two nitrifying systems treating the effluent from the anaerobic systems 3) the construction and start up of a denitrifying system to treat the effluent from one of the nitrifying systems, and 4) obtaining adsorption breakthrough curves utilizing diluted raw wastewater and and virgin carbon without the presence of biological activity. The progress of these efforts are depicted on the Gant Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.

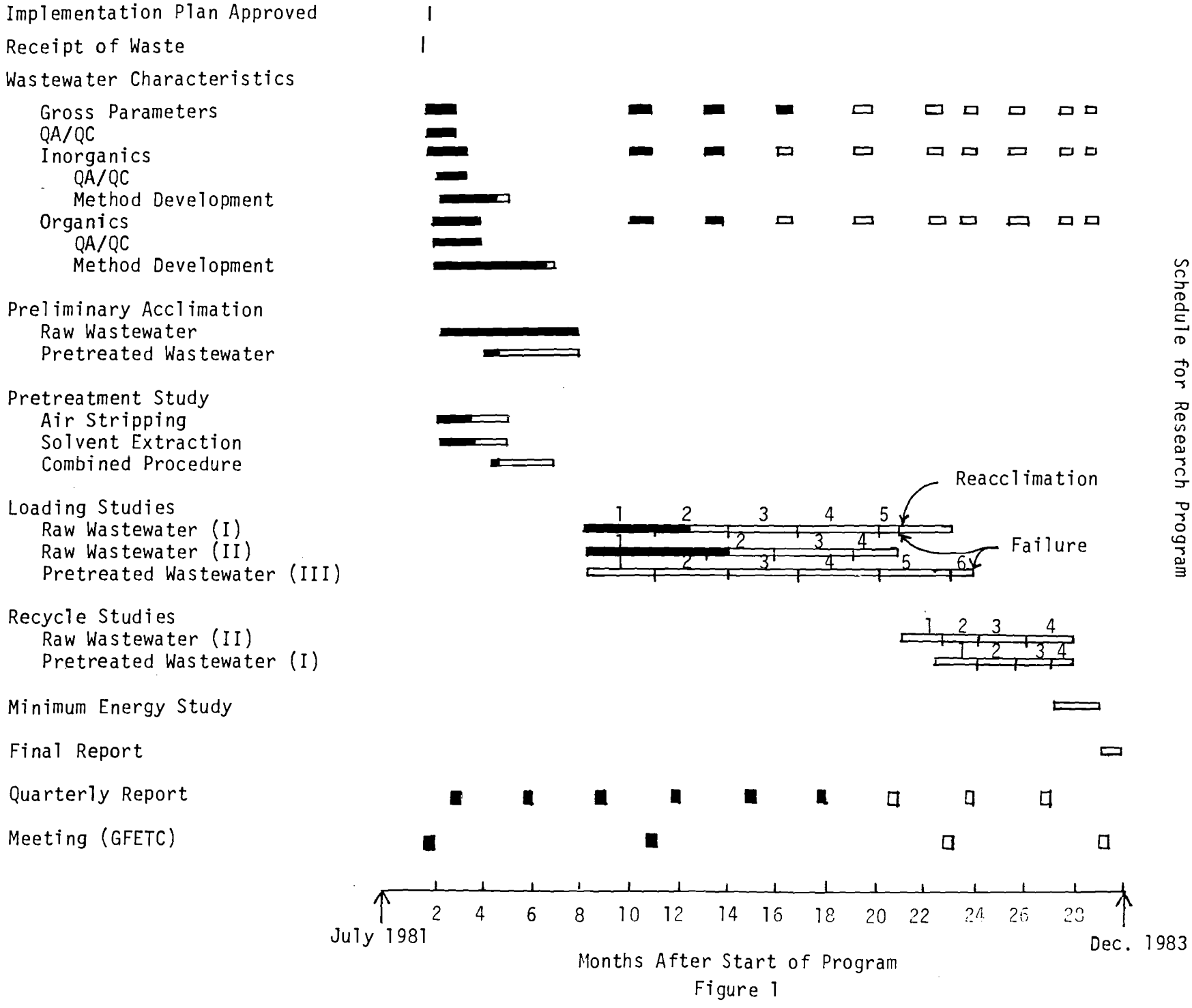
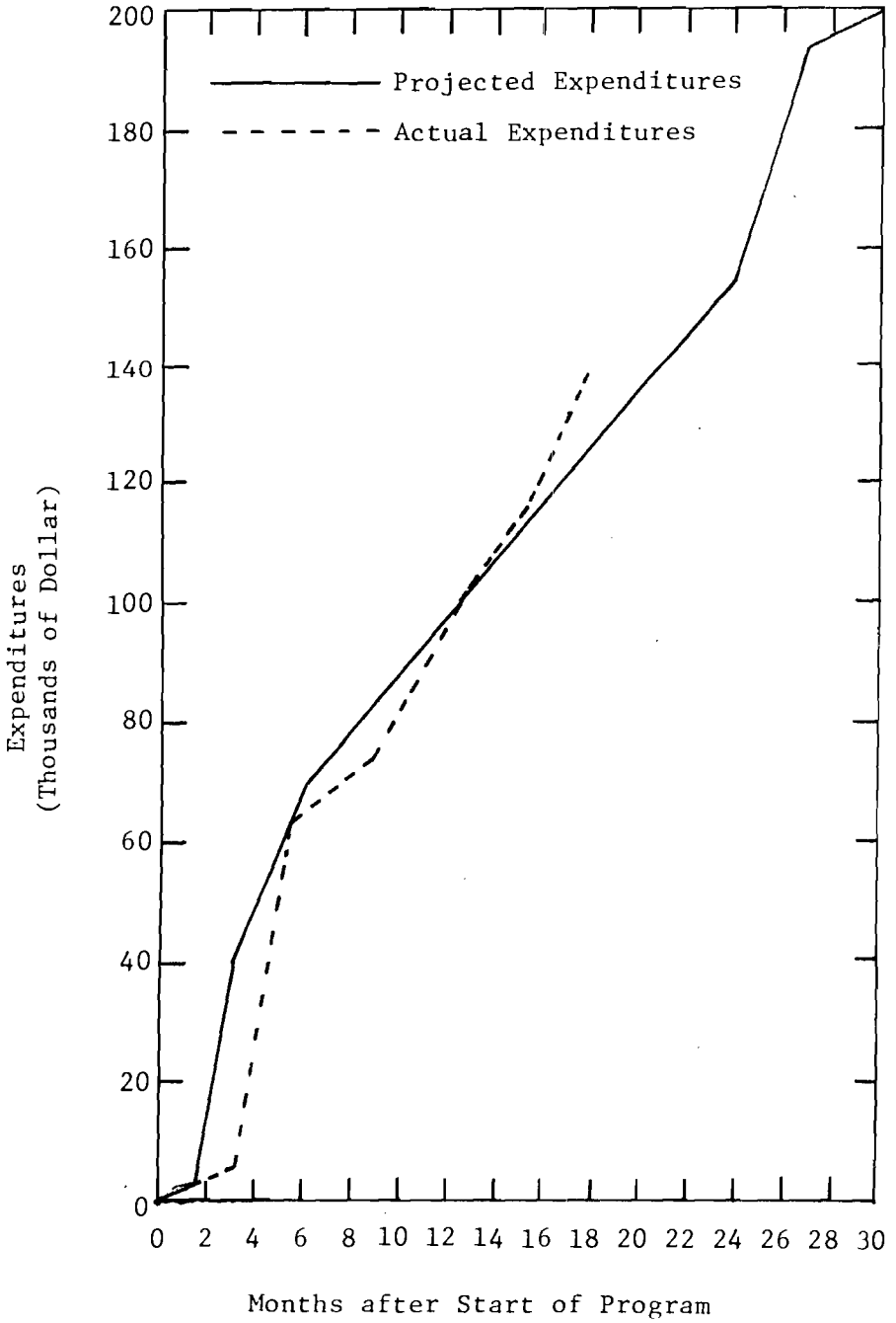

TASK
Implementation Plan Approved
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
Method Development
Preliminary Acclimation
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
2 4 6 8 10 12 14 16 18 20 22 24 26 28
July 1981
Dec. 1983
Months After Start of Program
Schedule for Research Program
2

Figure 1



Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

Figure 2.

II. ANAEROBIC TREATMENT SYSTEMS

A. Systems I and II

1. Operation

As indicated in the previous quarterly report (September 1982) these two systems were being redesigned and reconfigured for changes in operational strategy and have been taken out of operation.

Influent and effluent samples collected during the operational life time of these systems and the carbon contained within these systems is being more thoroughly analyzed for specific organic compounds. The results and interpretation of this data will hopefully furnish more insight into the constituent(s) which are responsible for the inhibition/toxicity to the biological system.

The above data and interpretation will be reported separately at a later date.

B. System III

1. Operation

System III has now been operating an additional 90 days (total operation 360 days) on ~10% raw wastewater at a flow of 10 ml/min.

2. Removal Efficiencies

System efficiency has continued to slowly decrease as can be seen in the data reported in Figures 3, 4, 5, 6, 7 and 8.

Figures 3 and 4 are plots of influent -effluent COD values and COD Removal, %, respectively for System III. As can be seen (Figure 3) the effluent COD from the activated carbon column has continuously increased while the influent value has remained relatively constant. This is also reflected in the COD Removal plot (Figure 4) which shows a continuous decrease in the % COD removed across the entire system. The average removal for the current reporting period is only 36.2%.

Figures 5 and 6 (Influent - Effluent TOC and TOC Removal, respectively) show the same trend with the effluent TOC from the activated carbon column steadily

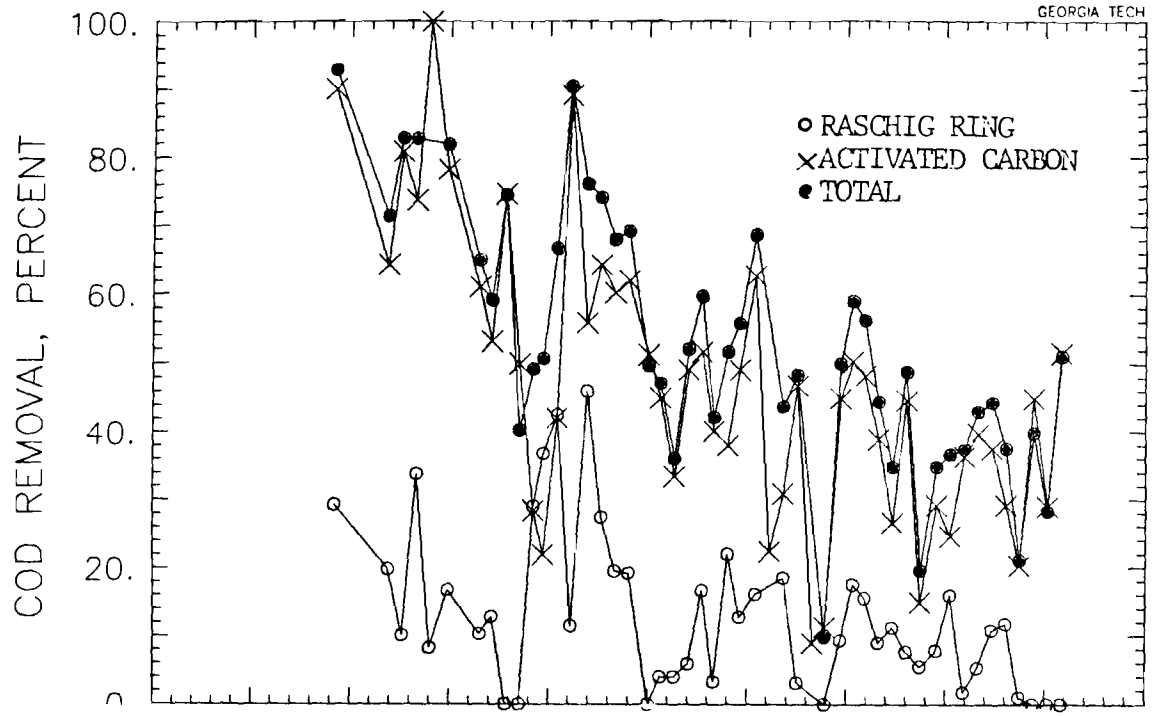


Figure 4

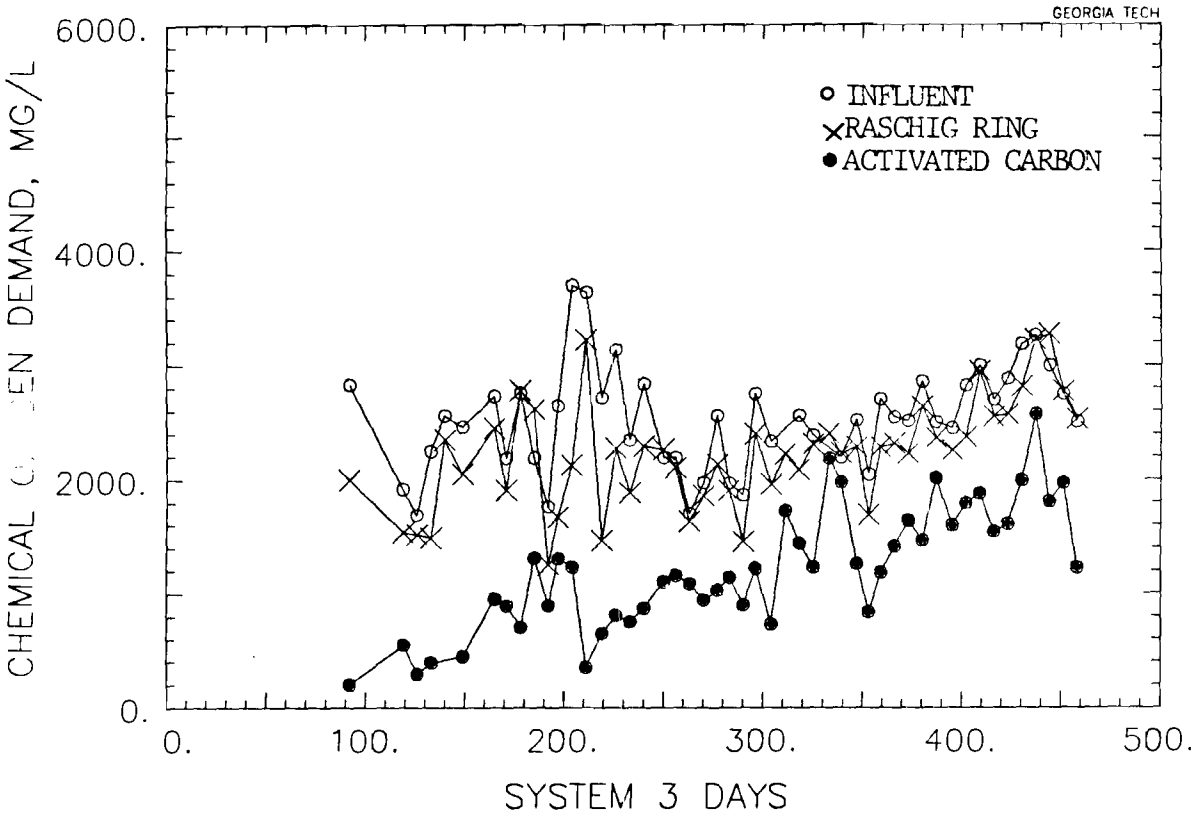


Figure 3

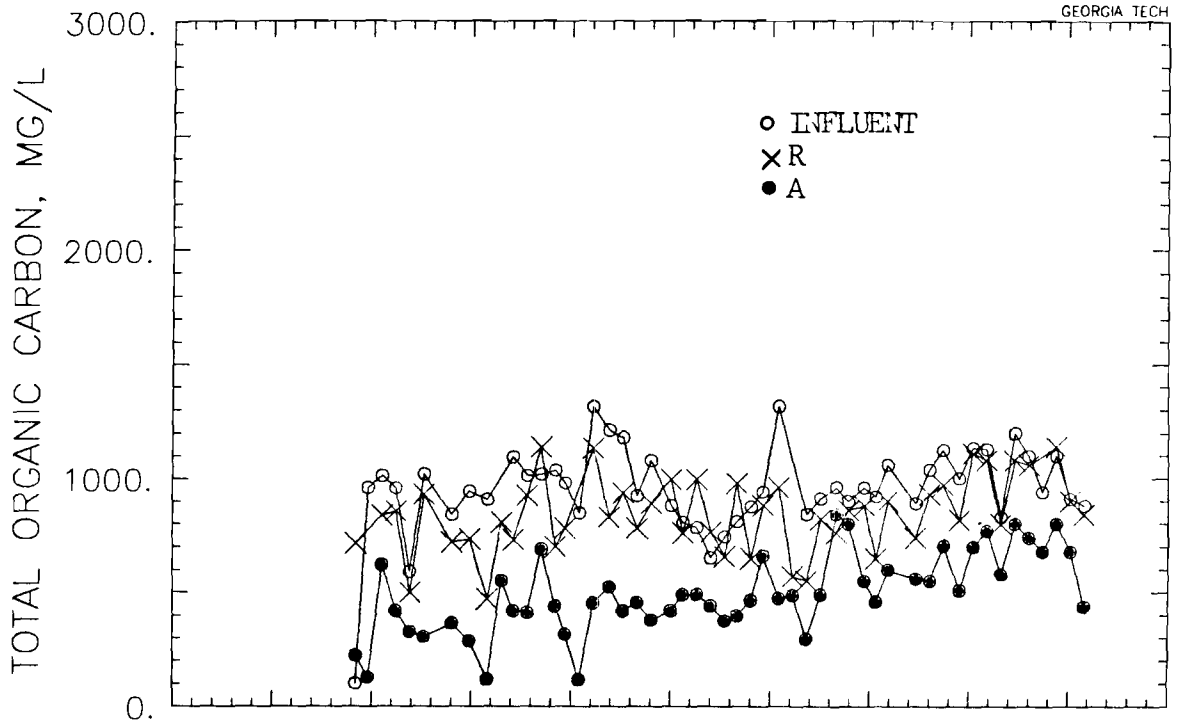


Figure 5

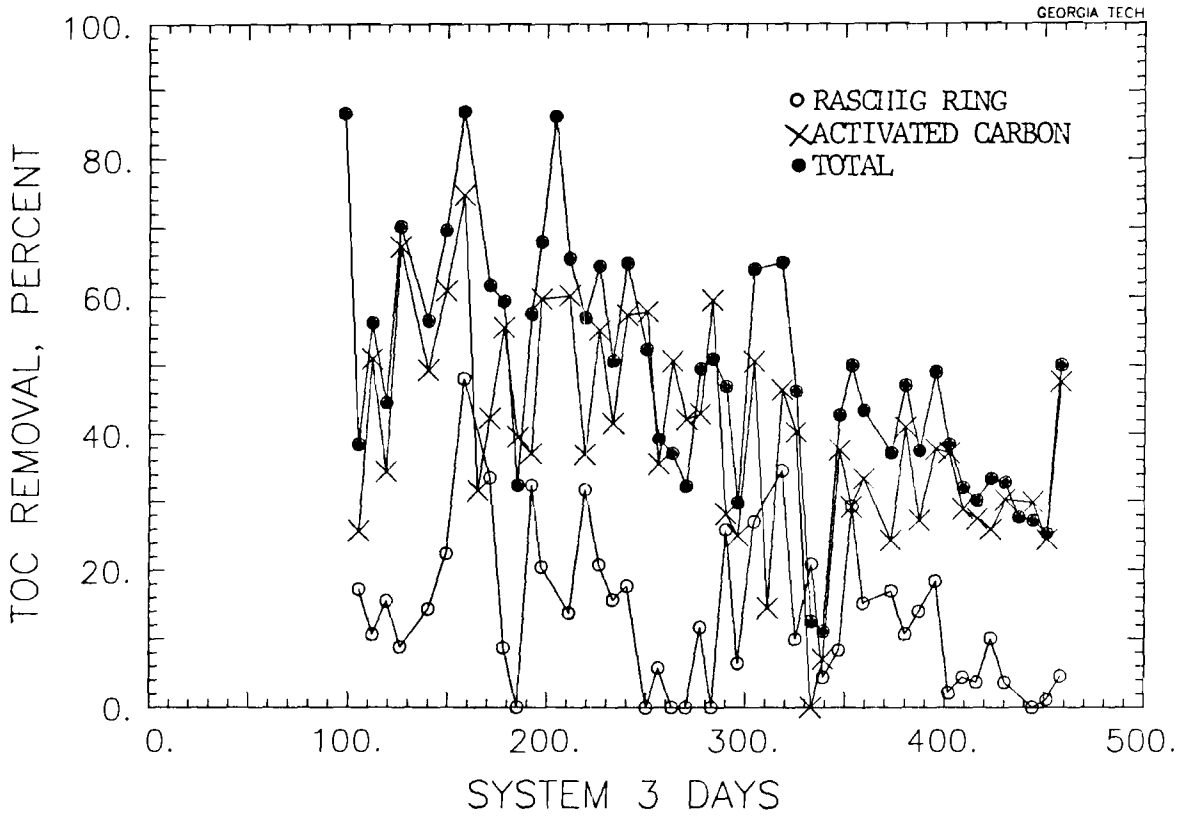


Figure 6

increasing results in a continuous decrease in the overall TOC removal across the system. TOC removal averaged only 35.2% for the period (day 367-451).

Influent - Effluent phenol concentrations and phenol removal, Figures 7 and 8 respectively reflect the same steady decrease in system performance. Phenol removal averaged 55.8% for the period.

The above removal percentages of 36.2, 35.2 and 55.8 for COD, TOC and phenol respectively compare to values of 44.4, 42.0 and 60.9 for the same parameters during the previous 90 days of operation (day 276-366).

3. Gas Production

The rate of gas production in System III has also decreased during the last 90 days of operation. Total gas production has averaged 5.6 1/day with an average methane content of 72.6%. This compares to values of 6.6 1/day and 77.2% methane reported for the previous 90 days of operation.

C. System IV

1. Operation

System IV (three activated carbon columns in series) has now been operated for a period of 65 days. The system has been operated on an influent consisting of ~10% raw wastewater at a flow rate of 5 to 10 ml/min. The flow rate has been periodically increased since the initial start up of the System. In addition the raw wastewater flow has been supplemented with effluent from System III in order to more rapidly establish biological activity in Columns B and C.

2. Removal Efficiencies

COD, TOC and phenol removal efficiencies across the system are extremely high because of the fresh granular activated carbon contained in columns B and C. TOC removals have ranged from 30 to 94% for the period with an average value of 69.5% while COD removals range from 64 to 94% with an average value of 86.5%. Phenol is being totally (100%) removed across the treatment system.

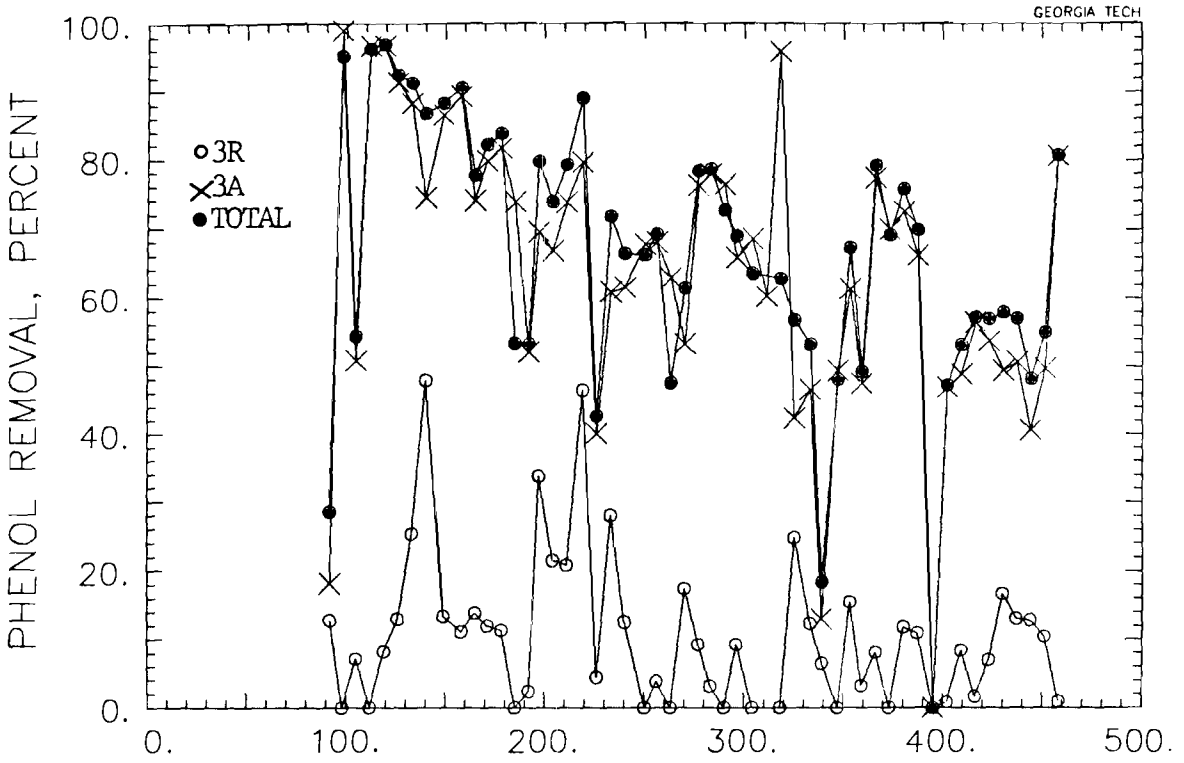


Figure 8

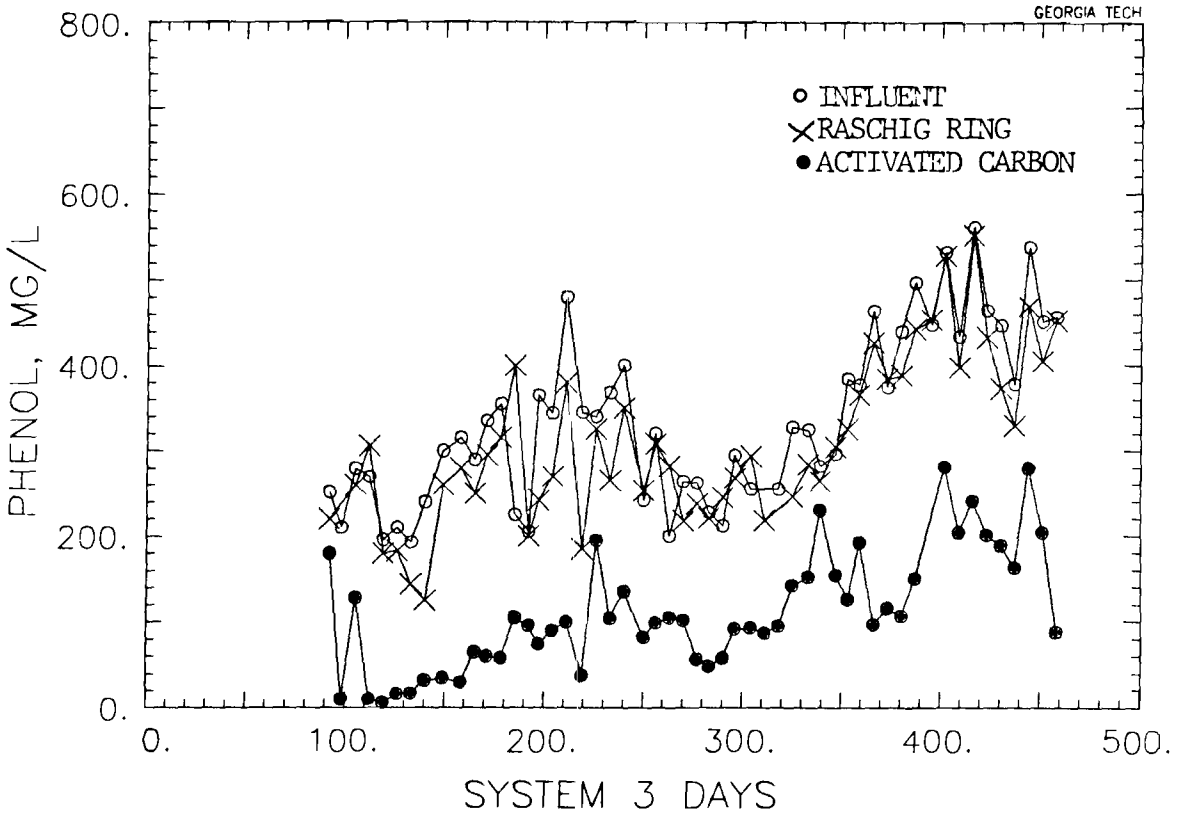


Figure 7

3. Gas Production

Methane production has steadily increased during the period of operation to a value of 1.9 l/day. The bulk of the methane (89%) is being produced in column A (the first column in the series) with the remainder being produced in columns B and C.

III. NITRIFICATION SYSTEM

A. AS and PAC-AS Systems

1. Operation

Currently two nitrification systems are being operated. The first system is being fed effluent from Anaerobic System III and is designated as the PAC-AS System while the second nitrifying system is being fed effluent from Anaerobic System IV and is designated as the AS System. Differences in operation and performance are discussed in the following section.

2. AS System

Due to the deteriorating quality of the effluent from Anaerobic System III the nitrification system then in operation showed signs of inhibition/toxicity with effluent ammonia values (Table 1) increasing rather rapidly during the period October 4 through November 16. To prevent the complete loss of biological activity one-half the contents of the reactor were transferred to a second reactor system. The original reactor (designated AS) was then used to treat the high quality effluent from Anaerobic System IV, while the new System (designated PAC-AS) was used in an effort to study the recovery of biological activity in the unit by addition of powdered activated carbon.

As can be seen from the ammonia data in Table 1 the AS unit rapidly recovered with the effluent ammonia concentration decreasing rapidly over a period of days. The AS system is continuing to operate on undiluted effluent from Anaerobic System IV and is converting greater than 99% of the ammonia nitrogen to nitrate, nitrite and organic nitrogen.

3. PAC-AS System

In order to determine if the effect of the inhibitory/toxic compounds in the effluent from Anaerobic System II could be successfully dealt with, a second nitrification reactor (designated PAC-AS) was put into operation. This unit

Table 1

Influent-Effluent Nitrogen Values
AS Nitrifying System

Date	NH_3, mg/l Inf.	NH_3, mg/l Eff.	NO_2^-, mg/l Eff.	NO_3^-, mg/l Eff.	Comments
10-4	520	30		466	Operating on System III Effluent
10-10	470	88		380	
10-19	510	85		180	
10-22	530	155		236	
10-27	600	425		33	
11-4	560	375		71	
11-11	570	460	28	36	
11-16	590	520	.3	18	One-half of MLSS removed. Began operating on System IV Effluent 11/17
11-22	425	313	2.3	115	
11-28	380	94	.6	295	
12-4	490	.7	.9	416	
12-11	535	.6	<.1	450	
12-18	520	1.5	45	490	
12-26	520	1.1	<.1	396	
12-30	520	.5	<.1	420	

utilized one-half the mixed liquor suspended solids from the original nitrification system for start up. Feed to the system consisted of effluent from Anaerobic System III plus powdered activated carbon (PAC). The purpose of the PAC was to adsorb constituents in the anaerobic effluent which were inhibitory or toxic to the nitrifying system.

Initial PAC dosing equivalent to 2000 mg/l PAC in the aeration basin had little effect on the system performance (Table 2 - 11/19 to 12/1). Increasing the dose to 3000 mg/l and diluting the anaerobic effluent 1:1 with water gave a rapid increase in unit performance (Table 2 - 12/11 to 12/28). The system is currently converting greater than 99% of the influent ammonia to nitrate, nitrite and organic nitrogen.

Table 2

Influent-Effluent Nitrogen Values
PAC-AS Nitrifying System

Date	NH_3, mg/l Inf.	NH_3, mg/l Eff.	NO_2^-, mg/l Eff.	NO_3^-, mg/l Eff.	PAC, mg/l	Comments
11-19	585	410	33	11	2,000	Operating on System III Eff.
11-25	570	398	42	23	2,000	
12-1	560	430	<.6	3	3,000	
12-11	283	208	22.5	25	3,000	Feed diluted 1:1 on 12/5
12-15	295	205	23	113	3,000	
12-22	330	183	26	153	3,000	
12-28	290	3.1	.1	247	3,000	
12-30	290	2.4	.1	260	3,000	

IV. DENITRIFICATION SYSTEM

Biological removal of nitrate-nitrogen is being examined using an upflow fixed-bed column system. The laboratory-scale column is packed with beryl saddles and is currently in an acclimation phase. Nitrified coal-gasification effluent is being applied to the column with excess methanol to develop an acclimated culture. Initial studies are to be focused on determination of methanol requirements by sequential reduction in influent methanol to an acclimated column at several loading conditions.

In conjunction with the attached-growth column system, a suspended-growth culture system is under development. While it is not yet operational it will contain an anoxic mixing basin followed by a small aeration chamber (for de-gassing) and a gravity sedimentation basin with sludge recycle to the initial anoxic basin. Determination of methanol requirements of an acclimated culture is to be accomplished initially.

V. COLUMN BREAKTHROUGH STUDIES

Figure 9 shows the results of a continuous flow breakthrough study performed using dilute wastewater and granular activated carbon in the absence of biological activity. The results indicate that without bioactivity the individual carbon columns used in the anaerobic systems would become saturated with phenol and cresols after 200 to 250 days of operation.

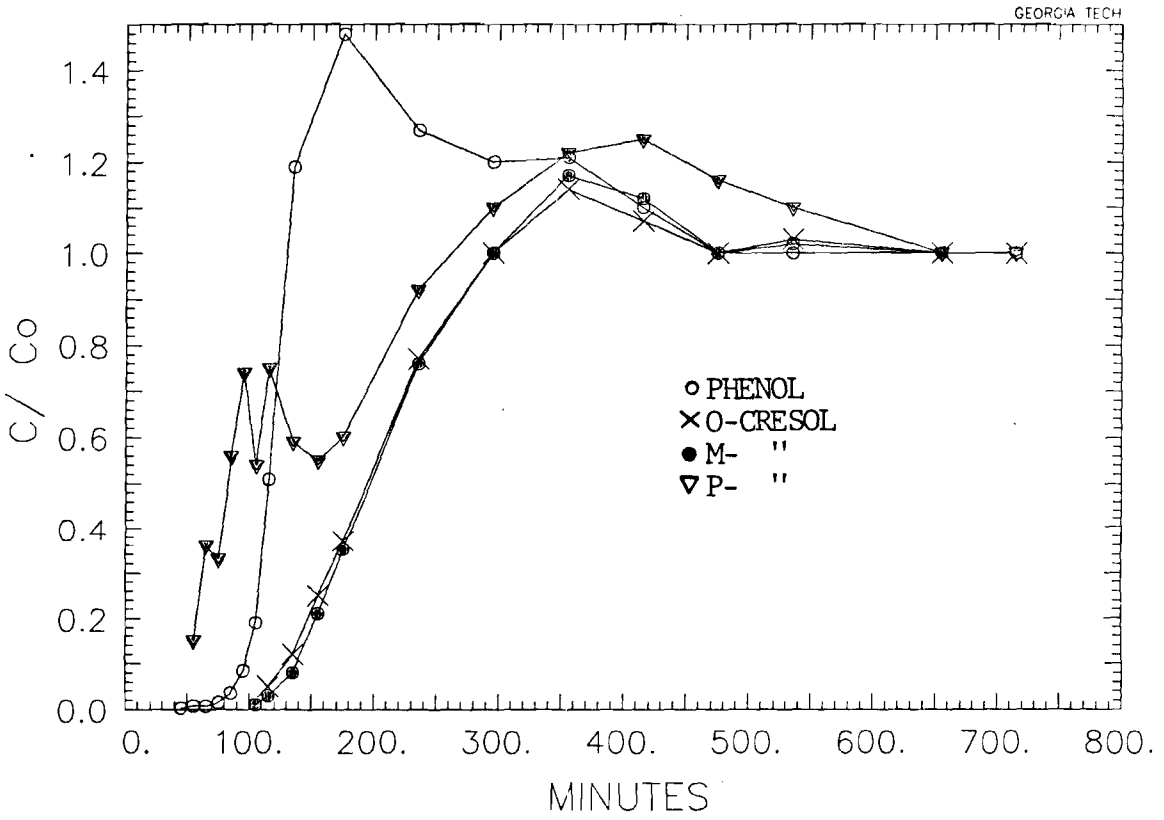


Figure 9. Phenol-Cresol Breakthrough Curve

VI. FUTURE WORK

System III, due to its decreased performance, will be operated on a carbon replacement basis in the coming quarter. Data from the breakthrough curves will be used as a basis for establishing a schedule for carbon replacement. Sufficient time will be allowed in the replacement schedule for biological stability to be attained between scheduled carbon removals and additions.

As soon as the anaerobic systems have attained pseudo steady-state operations, loadings will be increased to ascertain the maximum loading attainable without inhibition or toxicity to the biological system. During these studies the systems will be monitored for individual cresol concentrations as well as phenol and the other more general parameters such as TOC, COD, etc.

Analysis of exhausted carbon from Systems I, II and III will continue in order to identify as many compounds and determine the quantity removed from the wastewater by adsorption. Efforts will also be made to identify the compound(s) causing the inhibition/toxicity effect observed in both the anaerobic and nitrifying treatment systems.

Nitrification of the anaerobic effluents will continue in order to determine the maximum loading attainable and to furnish nitrified effluent for the denitrification system.

Denitrification studies will focus on operational parameters using methanol as a carbon source in order to optimize performance. Investigations will then be made into the use of pretreated wastewater as a carbon source for denitrification.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #11
March 1983

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TABLE OF CONTENTS

I. INTRODUCTION

This report summaries the work performed during the period from January 1, 1984 through March 31, 1984 on the DOE research program on "Anaerobic Treatment of Gasifier Effluent - Inhibition and Fate of Hydantoin Studies" (Contract No. DE-AC18-81FC10297). The major efforts have been directed towards: 1) continued operation of a continuous flow anaerobic system, 2) establishment of an anaerobic batch system, 3) initiation of serum bottle inhibition studies, 4) analytical methods development for hydantoin monitoring, 5) initiating a study on the aqueous stability of hydantoins, 6) initiating a study on the adsorption of hydantoins by granular activiated carbon, and 7) examination of samples from previously operating anaerobic system for indication of the possible fate of hydantoin.

II. ANAEROBIC TREATMENT SYSTEM

A. System III - Continuous Flow

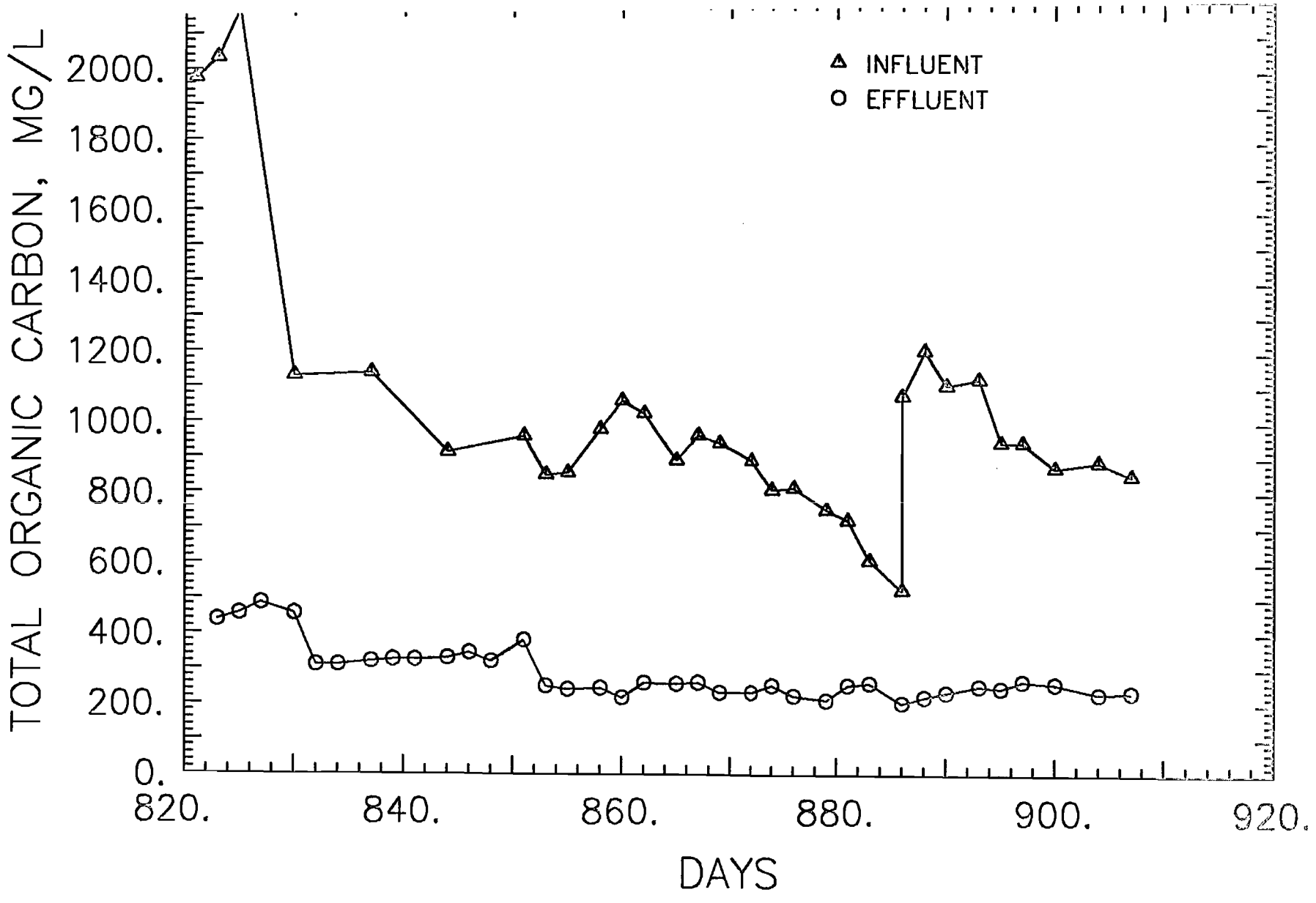
System III is still being operated as a continuous flow granular activated carbon expanded-bed filter. Influent to the system is ~10% raw wastewater at a flow rate of 5-10 ml/min (empty bed hydraulic retention time 24-48 hours). Partial carbon replacement is still being utilized with a replacement of 0.5ℓ (~5% of the carbon bed) every 10 to 21 days depending upon system performance. Organic removals in terms of TOC, COD, phenol and cresols (Figures 1, 2, 3 and 4) are quite good, however, gas production (Figure 5) is somewhaat more variable and is lower than what has been experienced previously. Gas composition is quite stable (Figure 6).

B. Batch System

A 10 L completely mixed tank reactor has been set up and is being operated on a draw and fill basis using diluted raw wastewater as the substrate. The contents of this system are to be used for seed in the serum bottle inhibition studies. This system is routinely monitored for TOC, COD, phenol, cresols, alkalinity and gas production and composition. Some difficulty has been encountered in obtaining stable gas production from the unit. Modification in the feed system for substrate introduction and the method of carbon replacement are being made to help alleviate this problem.

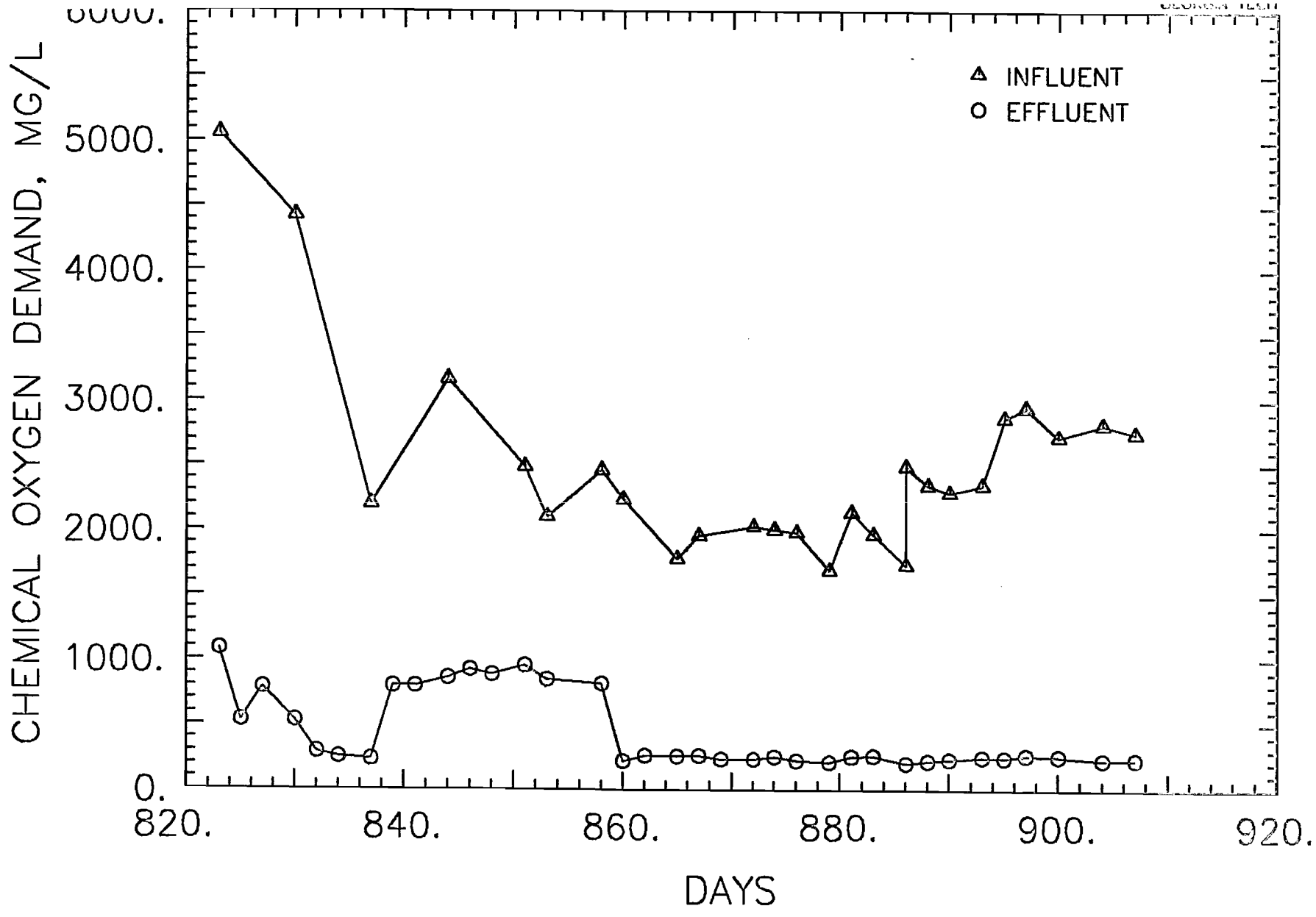
C. Serum Bottle Studies

Serum bottle studies have begun using the contents of the batch reactor as seed and spiking the seed with varying amounts of potential inhibitors. Several problems have become evident in the initial phases



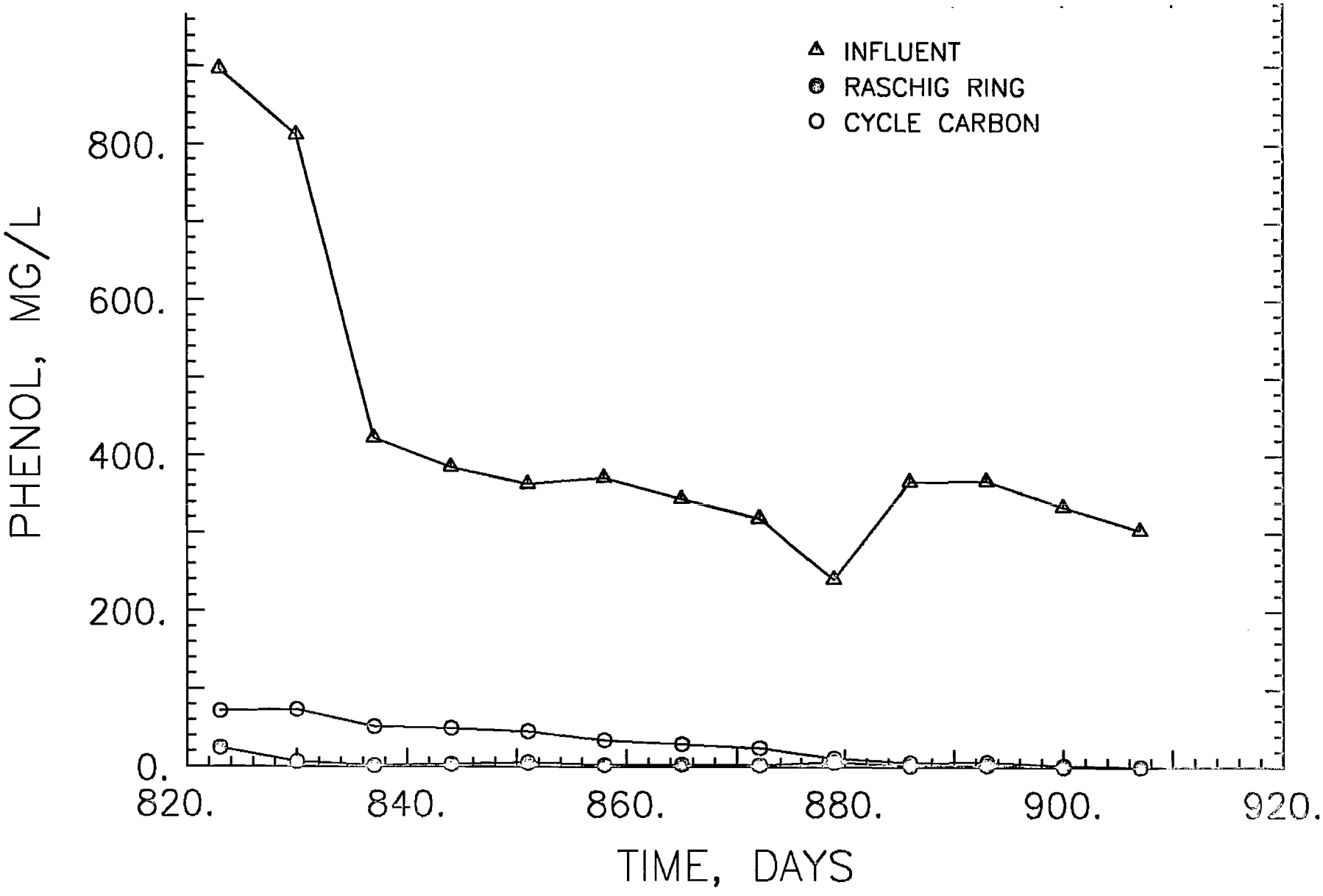
COLUMN 3A TOTAL ORGANIC CARBON

Figure 1



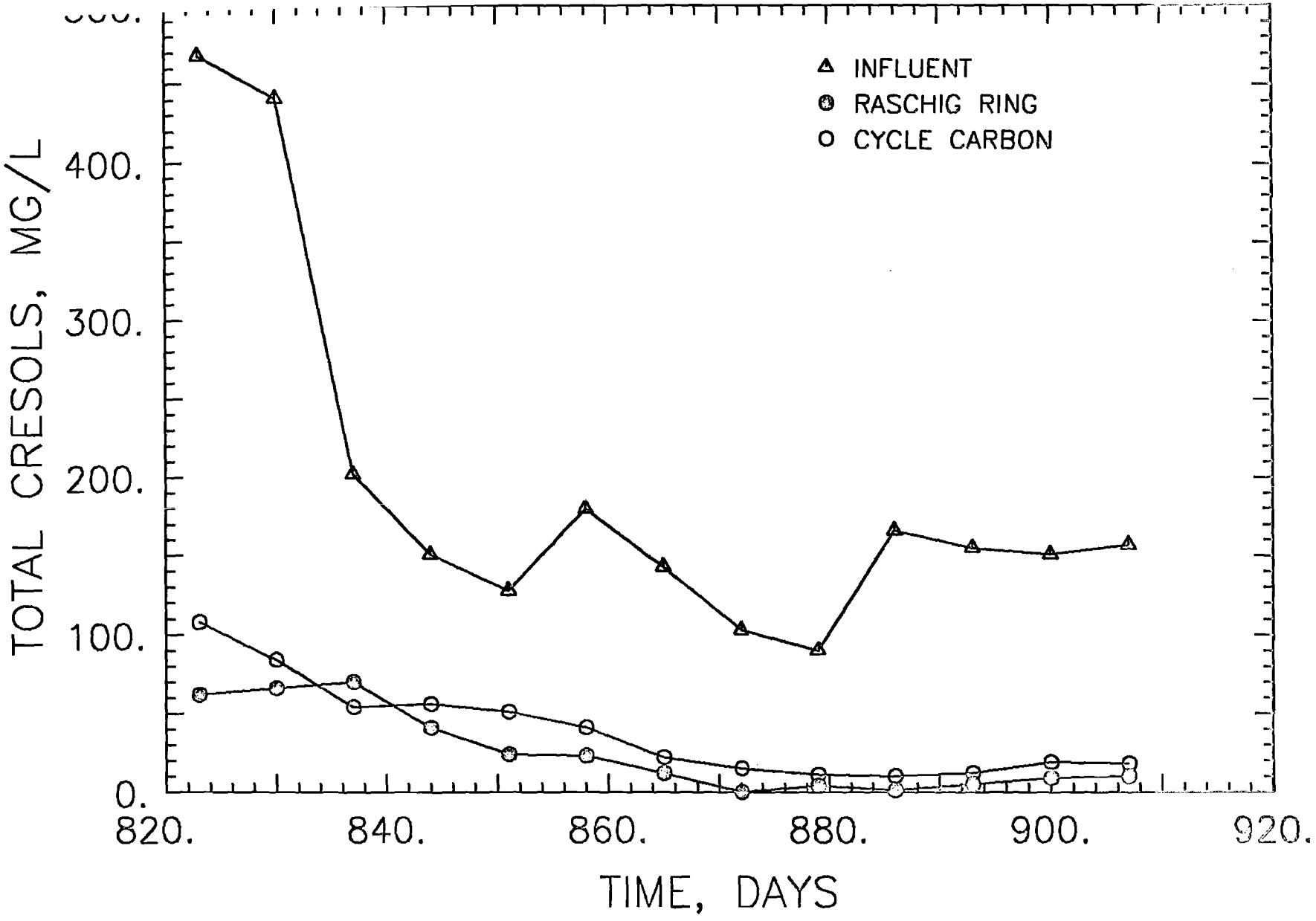
COLUMN 3A CHEMICAL OXYGEN DEMAND

Figure 2



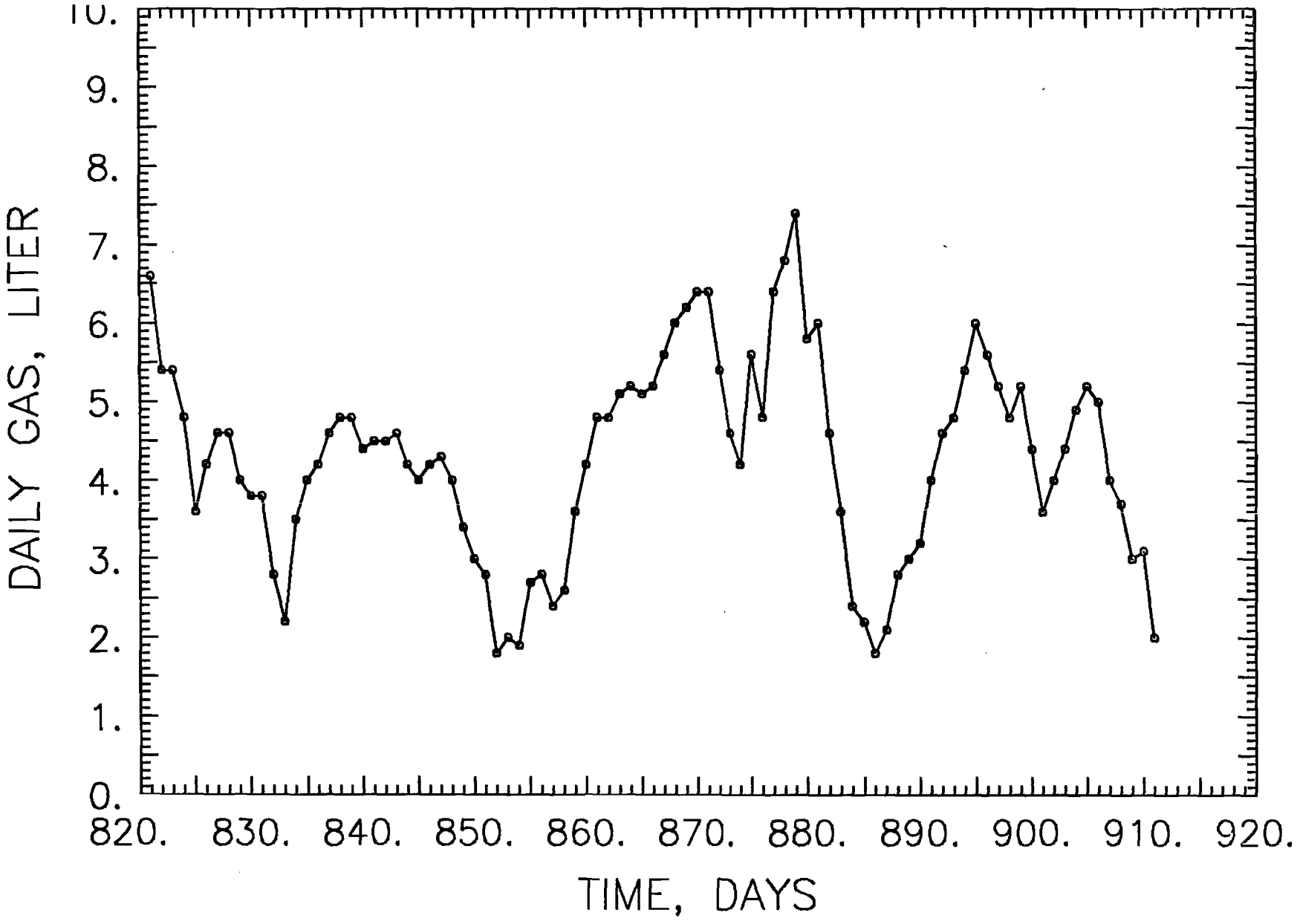
SYSTEM 3, PHENOL CONCENTRATION

Figure 3



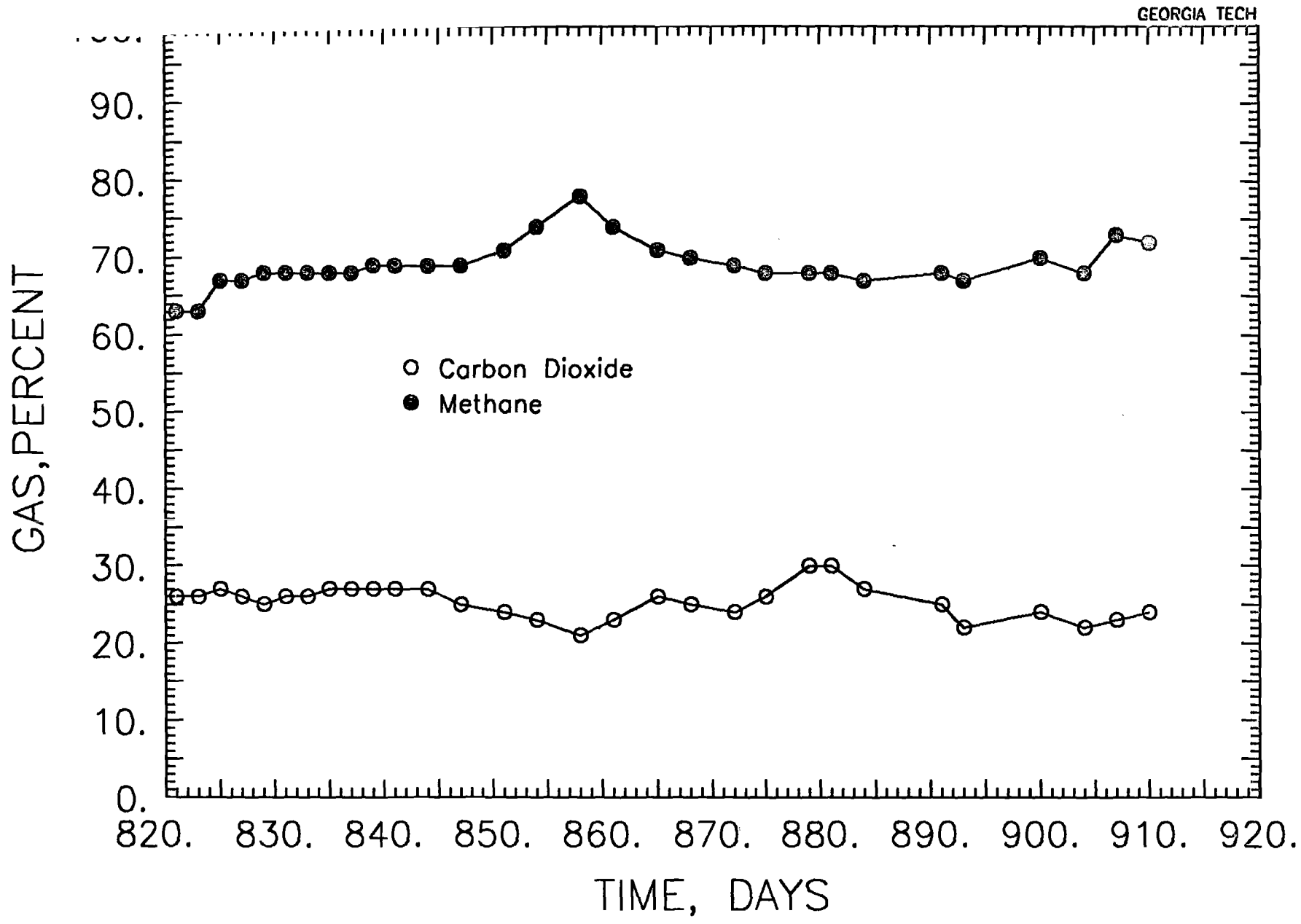
SYSTEM 3, TOTAL CRESOL CONCENTRATION

Figure 4



Gas Production of Column 3A

Figure 5



System 3 Cycle Carbon Column Gas Composition

Figure 6

of this effort.

The incubation time for maximum gas production which has been obtained has been extremely long, on the order of 60 to 75 days instead of 20 to 40 as reported in the literature. It is felt that this long incubation period is a result of at least two factors. One of these is the shock to the seed inoculum due to the transfer if strict anaerobic conditions are not maintained. The second is due to the variable and somewhat low gas production from the batch reactor. It is indicative of either poorly acclimated seed or a very low concentration of active organisms or both. However, this should not adversly effect the results of the serum bottle studies but rather only increase the time required to obtain the necessary data.

III. HYDANTOIN STUDIES

A. Analytical Methods

In order to monitor hydantoins for the carbon absorption and regeneration studies as well as in the biological treatment systems several possible methods of analysis have been investigated and are discussed individually in the following sections.

1. UV/VIS Spectroscopy

For samples containing only a single hydantoin and no other species which absorbs radiation in the 200-250 nm range, UV/VIS spectroscopy has been found to be applicable for analysis in the low mg/L range. Both 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin show adsorption maxima at 205-206 nm while hydantoin has an absorption maximum at 202 nm. The absorbtivities for the individual species are 2840 $\frac{L}{mole\text{-}cm}$, 2310 $\frac{L}{mole\text{-}cm}$, and 2400 $\frac{L}{mole\text{-}cm}$ for hydantoin, 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin, respectively. Using 1 cm cells the approximate detection limit for the individual compounds is in the 50 mg/L range and can be decreased to less than 10 mg/L by utilizing 5 cm cells.

2. Total Organic Carbon

Solutions containing only a single hydantoin species and no other organic compounds can be analyzed for the concentration of total organic carbon in the solution. The hydantoin concentration can then be calculated by use of the known molecular formula of the particular hydantoin. Experimental data show that the combustion-infrared method give quantitative conversion of the hydantoins to carbon dioxide. This allows for a very rapid analysis (approximately 5 minutes) of solutions containing only a single hydantoin species.

3. Gas Chromatography

Modification of the gas chromatographic/mass spectroscopy method developed at the Grand Forks Energy Technology Center has resulted in a direct aqueous injection technique for the analysis of 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin. The chromatographic column is a 6 ft. long by 2 mm i.d. glass column packed with 3% AT-1000 on chromasorb W-HP, 100-120 mesh. The column is conditioned overnight at 250°C. The analysis is done isothermally at 225°C using a flame ionization detector. Retention times are 8.8 and 10.7 minutes for 5-5-dimethylhydantoin and 5-methyl-5-ethyl-hydantoin respectively. Phenol, the cresols and all C_2-phenol isomers elute in less than 2 minutes and therefore do not interfer with the analysis. Estimated detection limits are on the order of 1 to 2 mg/L. As additional substituted hydantoins become available their retention times and detection limits utilizing this GC method will be determined.

4. Other Parameters

Solutions of individual hydantoins have also been evaluated utilizing other parameters commonly used in the assessment of wastes and wastewaters. Results from chemical oxygen demand (COD) analysis indicate less than complete oxidation of some hydantoins using the standard dichromate reflux method. Recoveries ranged from 70.0 to 96.8% with average recoveries of 73.8, 77.0 and 95.2% for hydantoin, 5,5-dimethylhydantoin and 5-methyl-5-ethylhydantoin, respectively. COD measurements therefore will be indicative of the concentration of hydantoins in solution but will give low values.

B. Aqueous Stability

A series of solution were prepared containing individual hydantoins at pH values ranging from 3 to 8. These solutions were stored in colorless glass bottles. One-half the solutions were exposed to incident sunlight while the other half were stored in the dark. Hydantoin concentration were measured periodically over a three month period, although, some of the solutions exposed to light showed visible amounts of algal growth, no significant changes in hydantoin concentrations were observed.

Samples of pretreated (solvent extracted - ammonia stripped) wastewater stored under refrigeration for periods of time as long as one year have been periodically analyzed and show no measurable change in hydantoin concentration.

C. Adsorption on Granular Activated Carbon

Preliminary experiments utilizing both individual hydantoins pretreated wastewater and raw wastewater show that hydantoins are adsorbed by granular activated carbon. Adsorption, with large doses of carbon, is complete when solution of individual hydantoins are used. However, in pretreated and raw

wastewater incomplete removal is observed apparently due to the competitive effects of other solutes in these more complex systems.

D. Analysis of Sample from Prior Anaerobic Studies

Selected samples from the System III anaerobic filter have been analyzed for hydantoins. Data obtained to date indicate partial removal of the hydantoins by the anaerobic system. However, the quantity and quality of the data does not allow a determination of the removal mechanism(s) at this time.

IV. FUTURE WORK

Serum bottle studies will be continued to ascertain which of the selected compounds under investigation are inhibitory to the anaerobic system. Attempts will be made to improve the performance of the batch reactor in order to decrease the length of time required to carry out a serum bottle assays. Carbon adsorption studies are continuing utilizing individual hydantoins in order to determine both the adsorption rate and the capacity of the granular activated carbon for hydantoins. In addition, a continuous flow column study using pretreated wastewater will be carried out based on the pure compound studies. Solvent regeneration of spent activated carbon will also be attempted when the carbon capacity data becomes available. Continuous flow anaerobic treatment studies with carbon replacement will be continued. As data on inhibition and/or hydantoin adsorption and removal becomes available the operation of the system will be varied in order to optimize the treatment performance. In addition, a single upflow anaerobic column containing ceramic media will be started and utilized to determine if the pretreated wastewater is amenable to anaerobic biodegradation without carbon adsorption.

E20-685

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #7
April 1983

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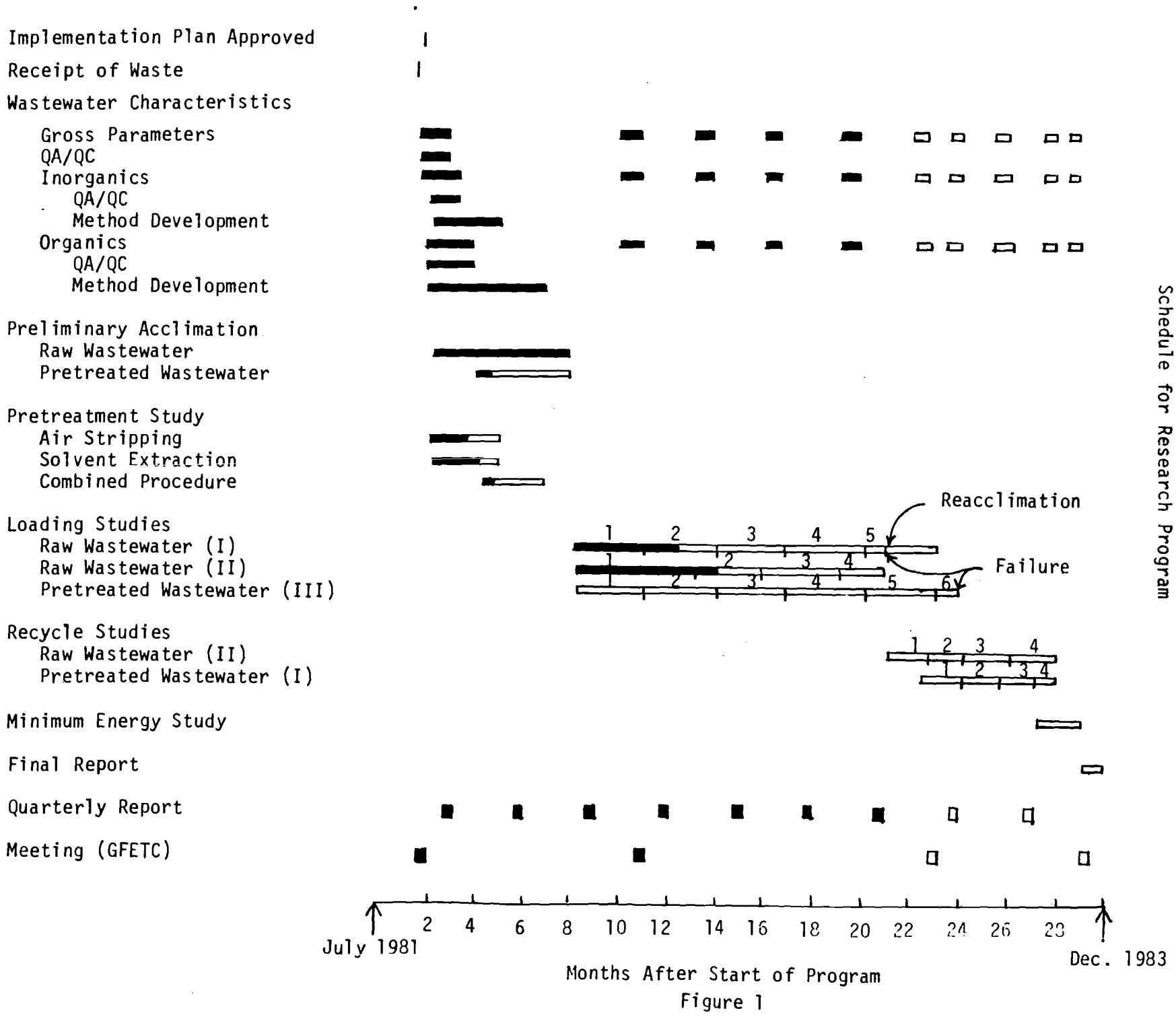
TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed during the period from January 1, 1983 through March 31, 1983 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward: 1) the operation of two anaerobic systems treating ≈10% strength raw wastewater with activated carbon replacement occuring in one system, 2) the operation of two nitrifying systems treating the anaerobic effluent, 3) the operation of both packed bed and suspended growth denitrifying systems for treating the effluent from the nitrifying systems, 4) completion of the GC/MS analysis of the spent activated carbon removed from previously operated anaerobic system, and 5) a brief, ultrafiltration - reverse osmosis, study on denitrified effluent to ascertain the feasibility of dissolved solids and trace organics removal. The progress of these efforts are depicted on the Gannt Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.


TASK
Implementation Plan Approved
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
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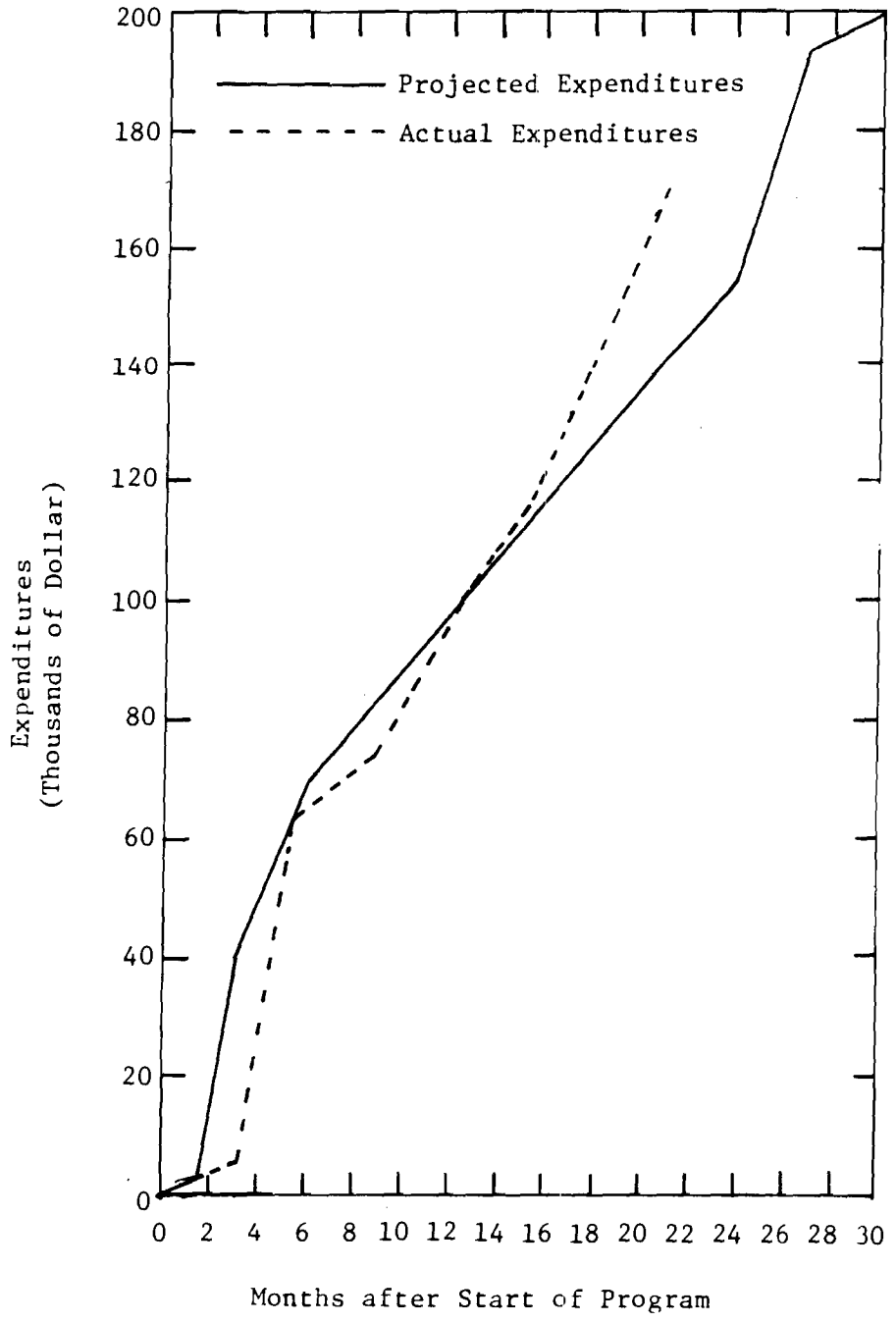
Preliminary Acclimation
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
July 1981
Dec. 1983
Months After Start of Program
Schedule for Research Program
Figure 1



Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

Figure 2.

II. ANAEROBIC TREATMENT SYSTEMS

A. System III

1. Operation

System III has now been operating an additional 90 days (total operation 450 days) on ~10% raw wastewater at a flow of 10 ml/min. Due to the continued decrease in removal efficiencies and gas production reported previously (Quarterly Report #6, December 1982) a program of replacement of a fraction of the granular activated carbon in the system was begun. This effort has met with some success as shown in increased removal efficiencies and gas production as indicated in the following figure.

Carbon replacement was carried out utilizing the following schedule: 1) addition of 1 liter (~400g) of fresh carbon to the operating system on day 456, 2) removal of 3 liters (~1200g) of spent carbon and addition of 2 liters (~800g) of fresh carbon on day 488, and 3) removal of 4 liters (~1600 g) of spent carbon and addition of 4 liters (~1600g) of fresh carbon on day 528.

2. Removal Efficiencies

As can be seen in Figures 3, 4 and 5 (COD, TOC and cresols, respectively) following each addition replacement of spent carbon there was an immediate decrease in effluent values for the above parameters followed by a slow increase toward their previous values. This decrease in effluent concentration could be attributed to immediate physical adsorption of the organics on the fresh carbon followed by slow saturation of the carbon and subsequent breakthrough of the organic compounds. However, concomitant with the increased organic removal efficiencies there was also a rapid increase in gas production as shown in Figure 6 indicating an increase in biological activity. This increase in biological activity could be attributed to either a decrease in concentration or

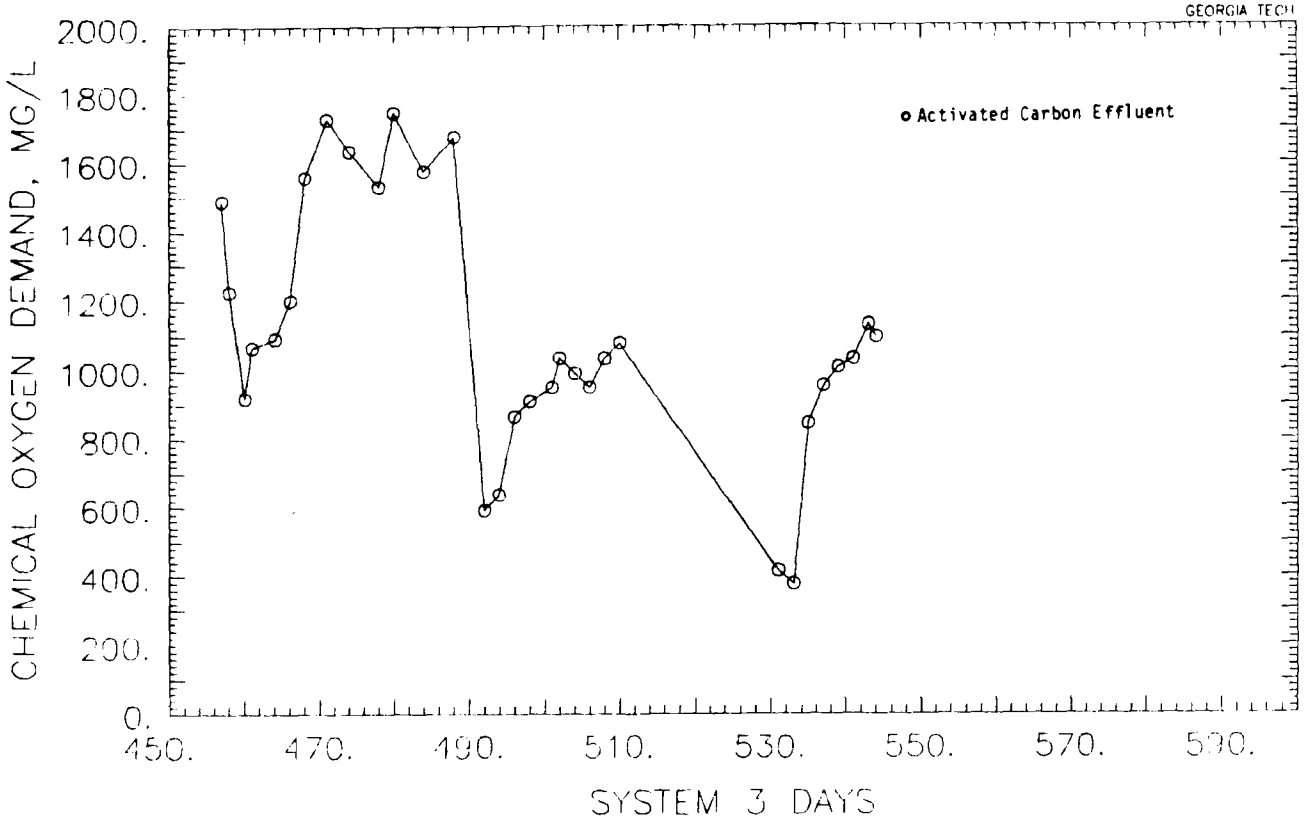


FIGURE 3

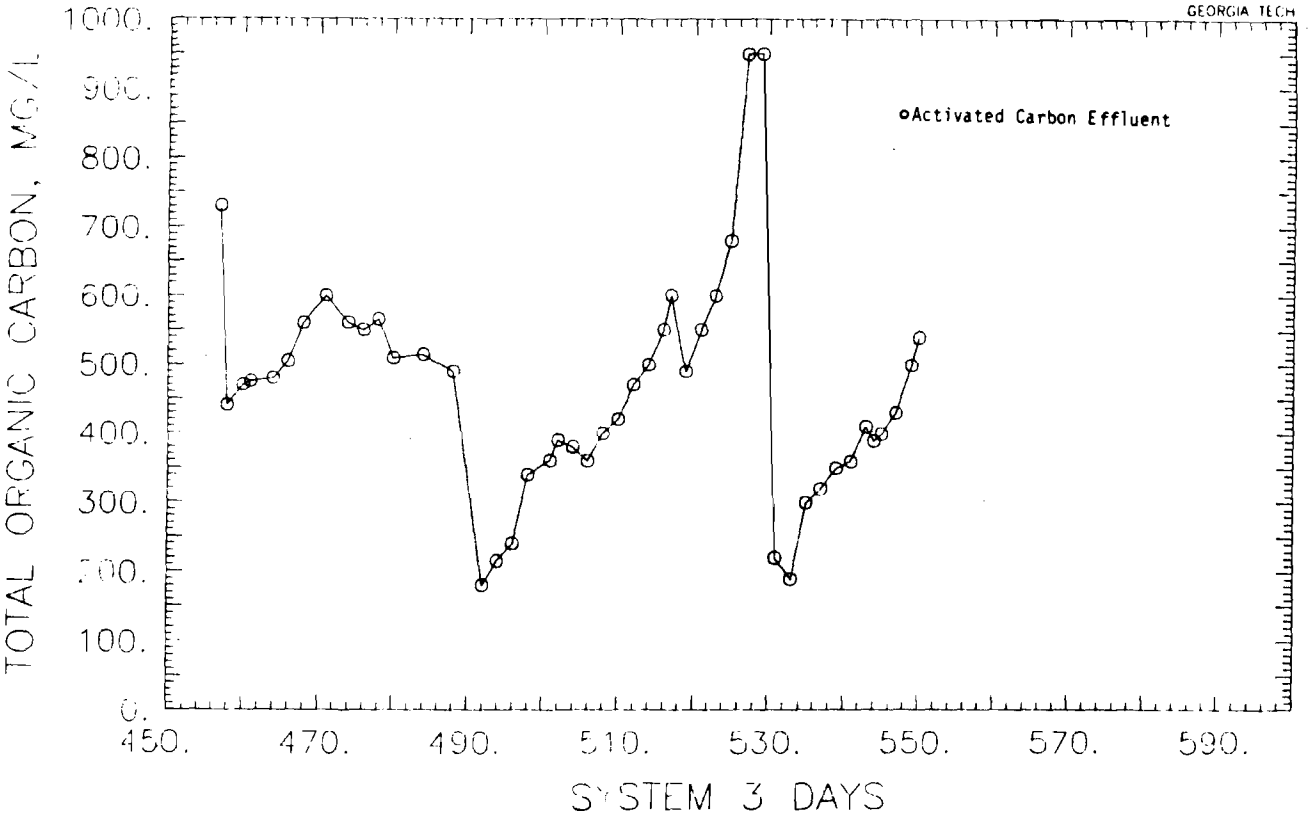


FIGURE 4

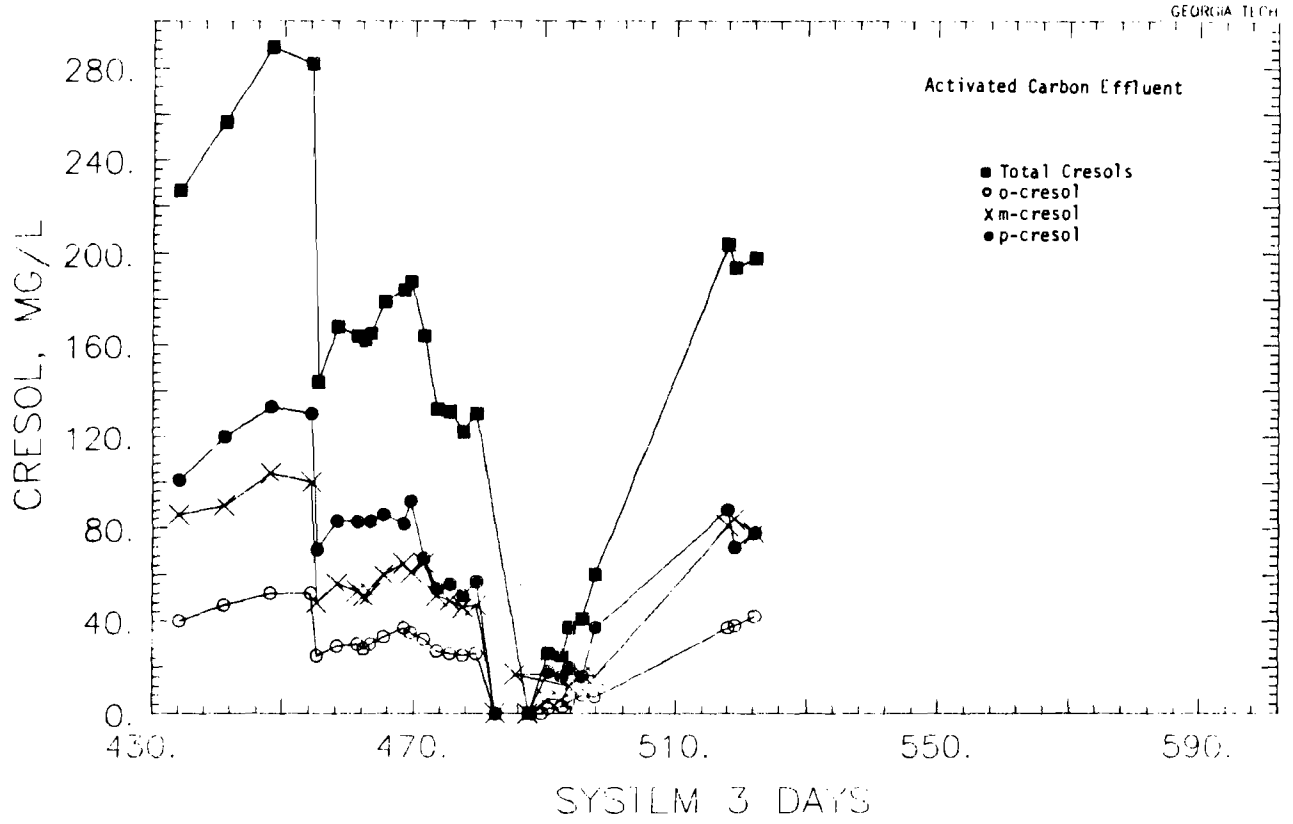


FIGURE 5

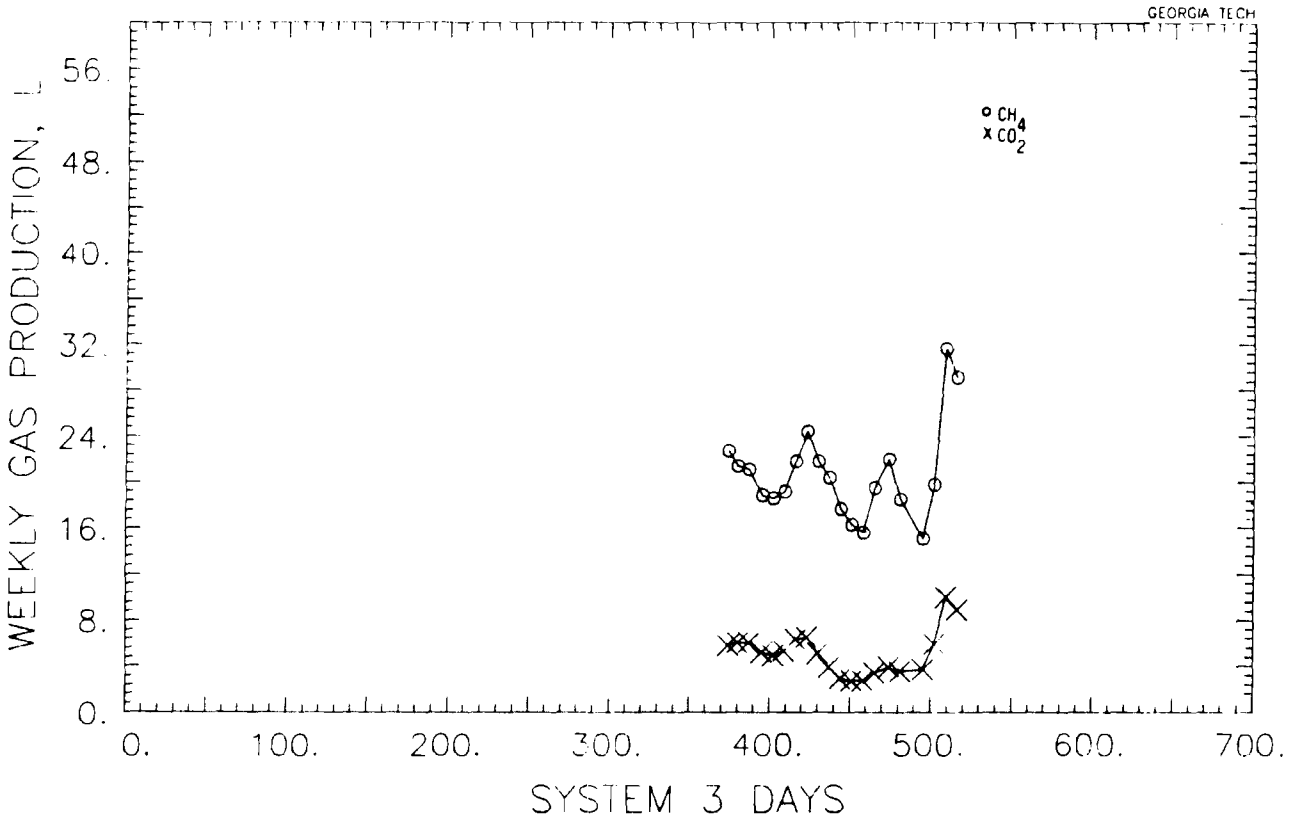


FIGURE 6

the removal due to adsorption of some compound or compounds which are inhibitory to the biological system. Overall removal efficiencies for COD increased from 36% prior to carbon addition/replacement to 59, 74 and 70% respectively after each subsequent change in carbon. The corresponding TOC removals efficiencies were 35% prior to carbon replacement and 53, 76 and 69% respectively after each carbon replacement. Phenol removal increased from 56% to 81, 88 and 94% respectively after each carbon addition.

3. Gas Production

Gas production averaged 5.6 ℓ/day before carbon addition/replacement was begun. The maximum gas production values were 5.6 ℓ/day, 7.0 ℓ/day and 9.8 ℓ/day respectively after each carbon addition/replacement.

4. Cyanide and Sulfide

Cyanide and Sulfide are being monitored in the system for production and/or removal in order to assess their potential for inhibition of the system. As can be seen in Figure 7 the sulfide increases indicating reducing conditions within the system and conversion of either sulfate or organic sulfur compounds to sulfide. At the same time (Figure 8) cyanide shows a decrease in concentration across the system indicating either some bioremoval or more likely adsorption onto the activated carbon.

B. System IV

1. Operation

System IV has now been operated for a period of 155 days. During the past 90 days it has been operated on the same influent as System 3 and at an identical flow rate, 10 ml/min, with no other supplemental feed.

2. Removal Efficiencies

COD, TOC and phenol removal efficiencies across the system remain relatively high because of the relatively short time this sytem has been operated. However,

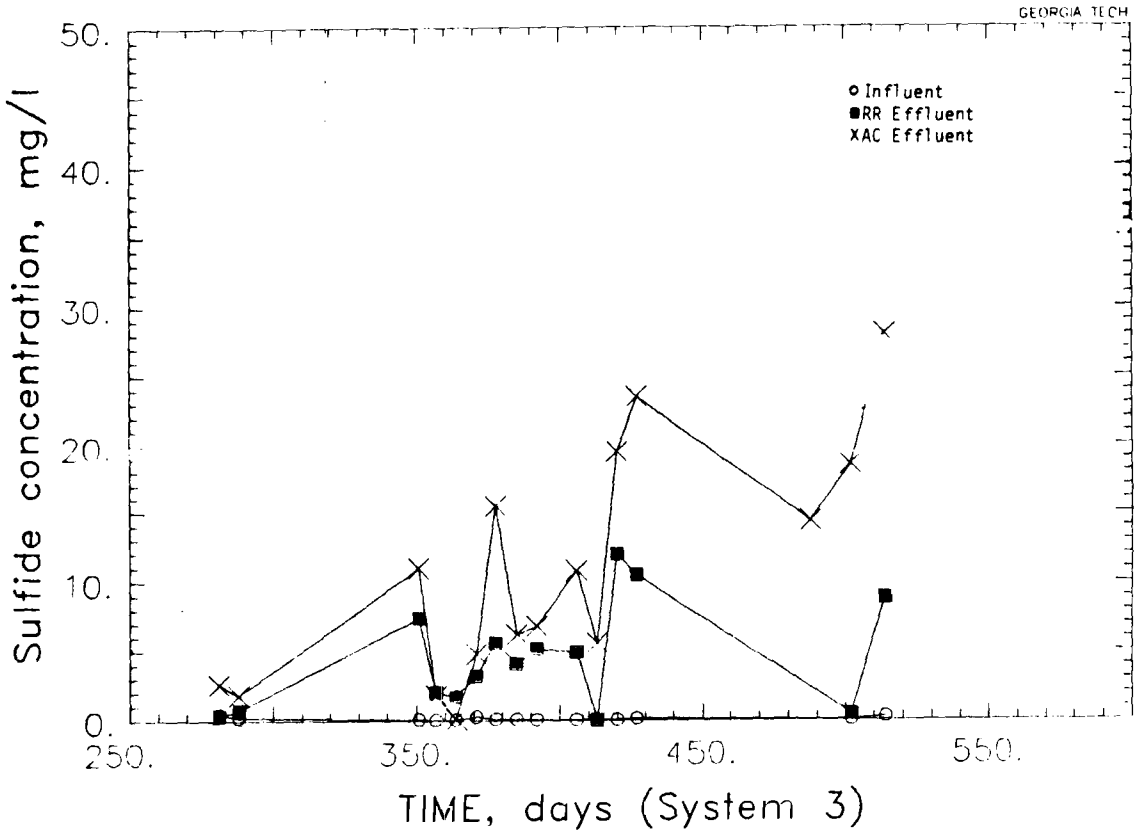


FIGURE 7

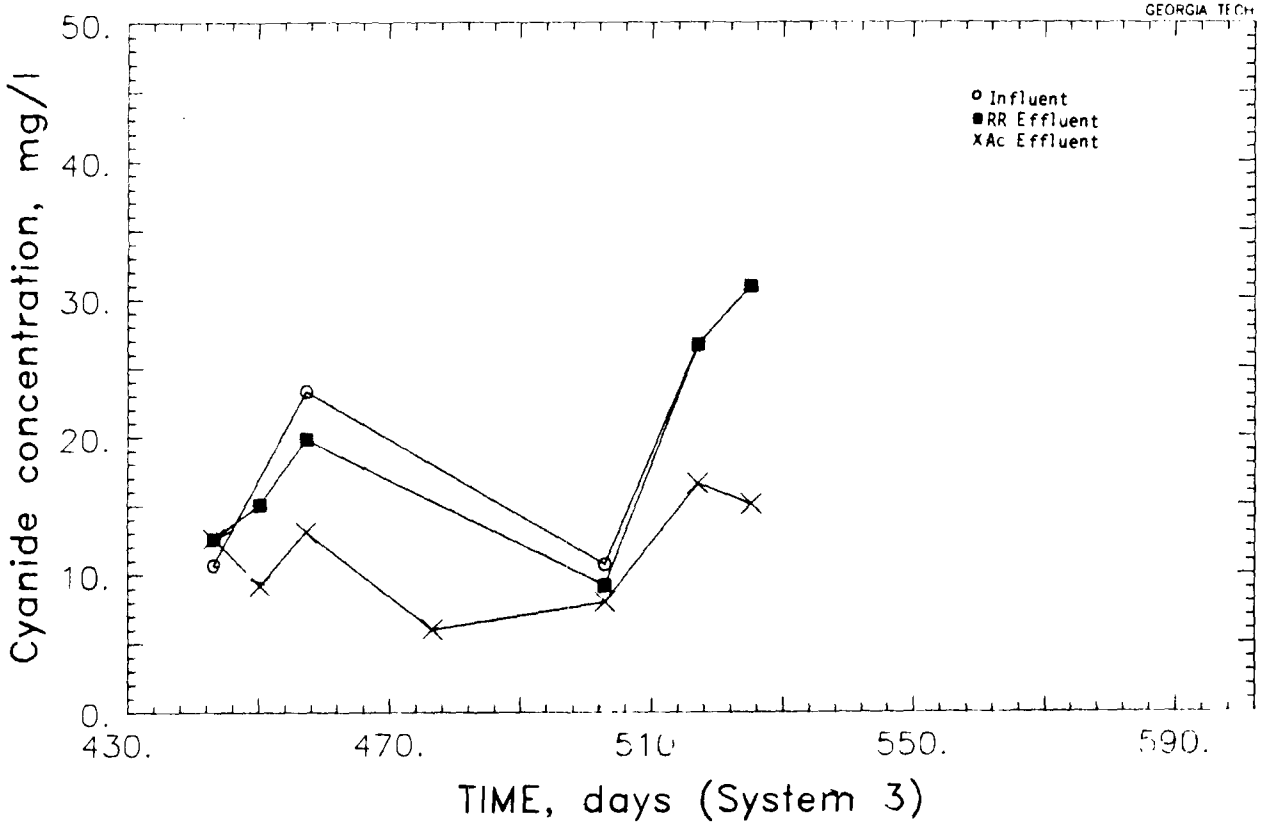


FIGURE 8

it appears that a slight decrease in removal efficiency is occuring. TOC removals have ranged from 75 to 95% for the period with the lower removals occuring during the last few weeks of operation. COD removals follow the same pattern with a range of 79 to 95%. Phenol removal is still complete in the overall system but there are measurable concentrations (10 to 80 mg/ℓ) in the effluent from column B. These data trends can be observed in Figures 9, 10 and 11.

3. Gas Production

Gas production remains fairly low in the system with the majority of the gas still being produced in solumn A. The production rate is increasing as can be seen in Figure 12 with maximum production of 2.7 ℓ/day.

4. Sulfide and Cyanide

As with System III sulfide is being produced in System IV while cyanide is being removed. Figure 13 and 14 show sulfide and cyanide concentrations respectively across the system.

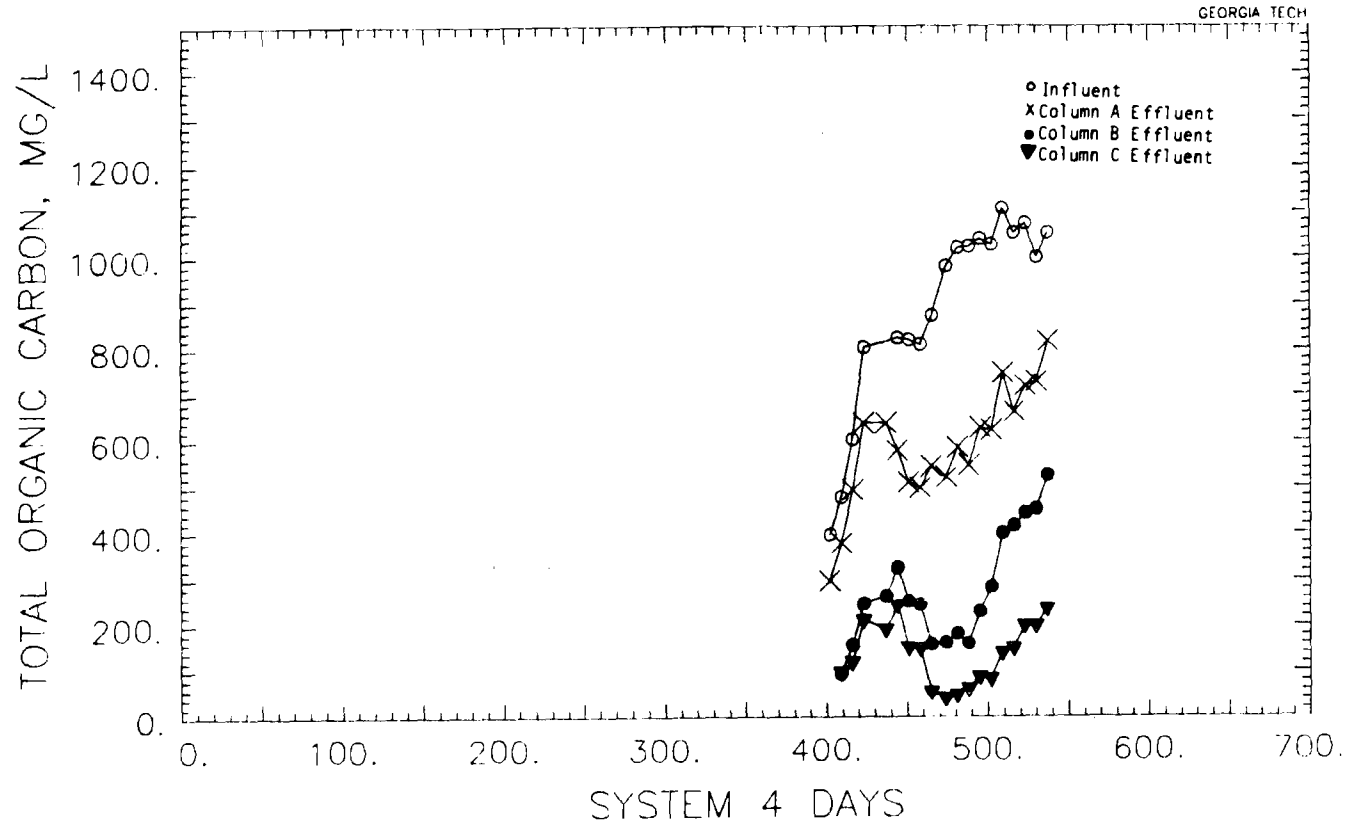


FIGURE 9

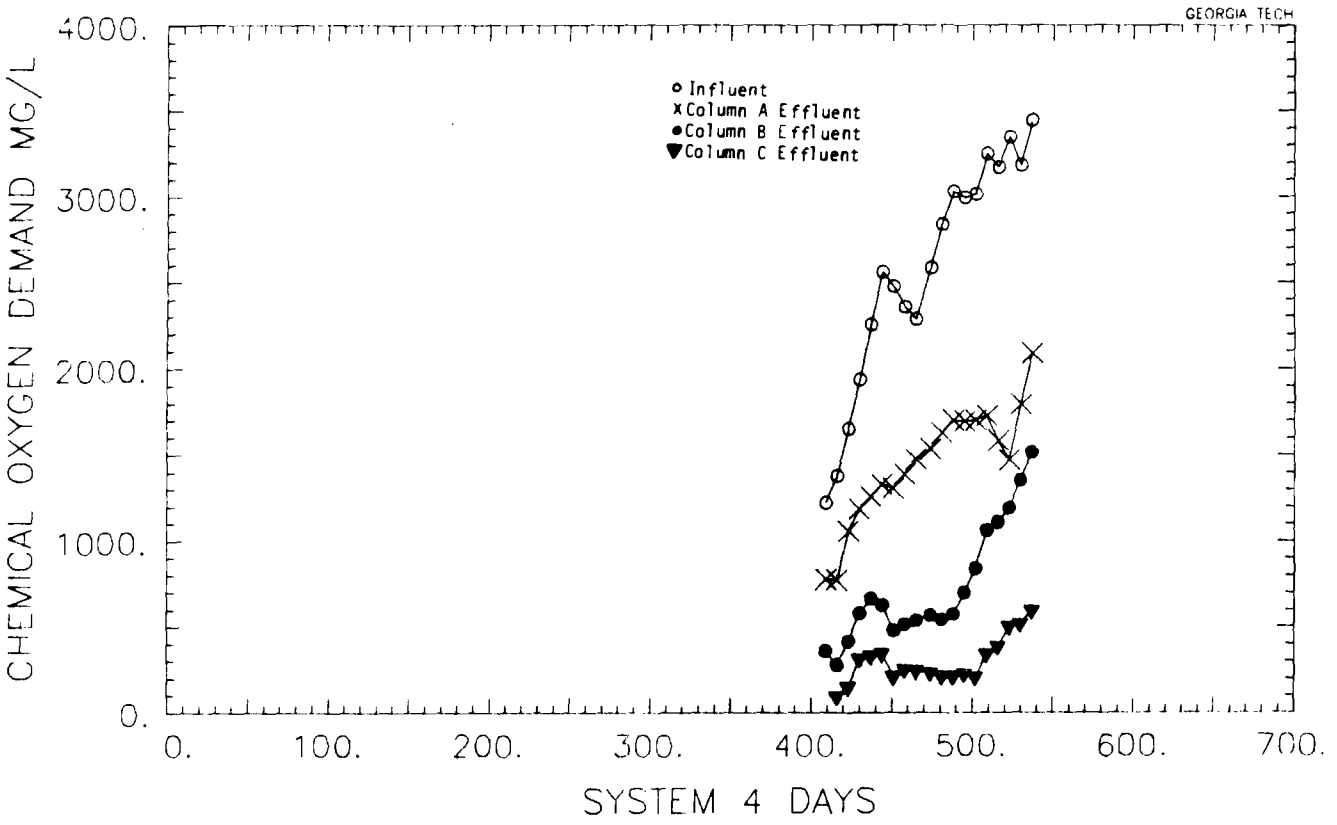


FIGURE 10

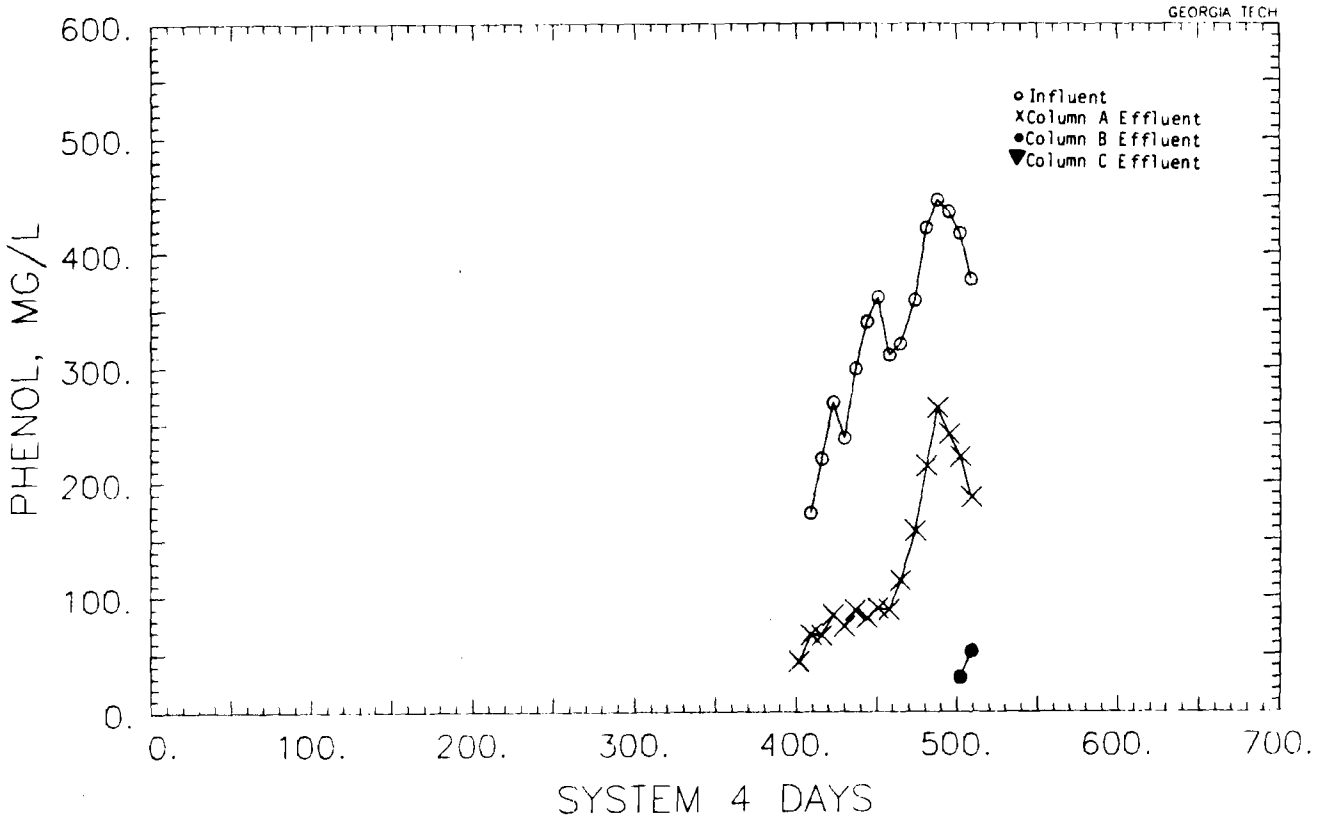


FIGURE 11

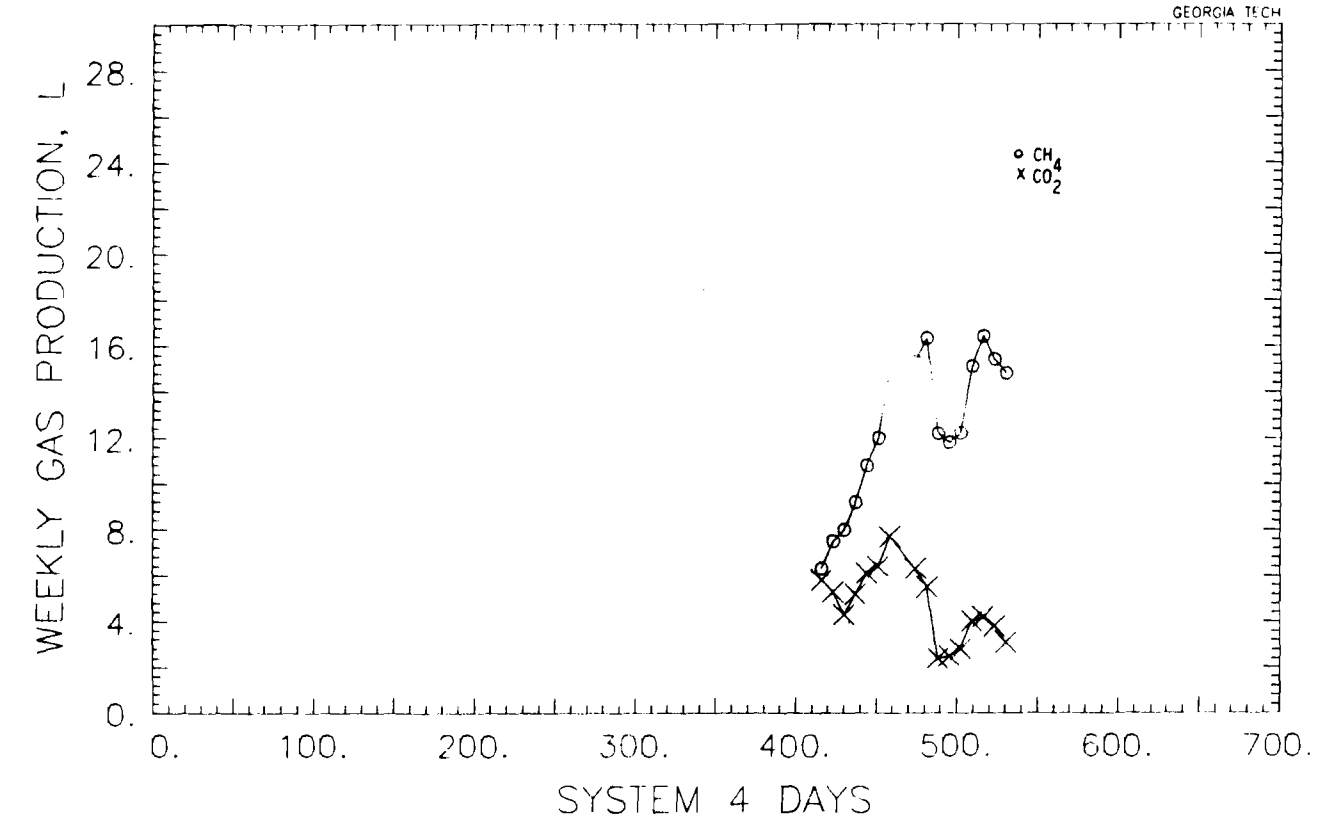


FIGURE 12

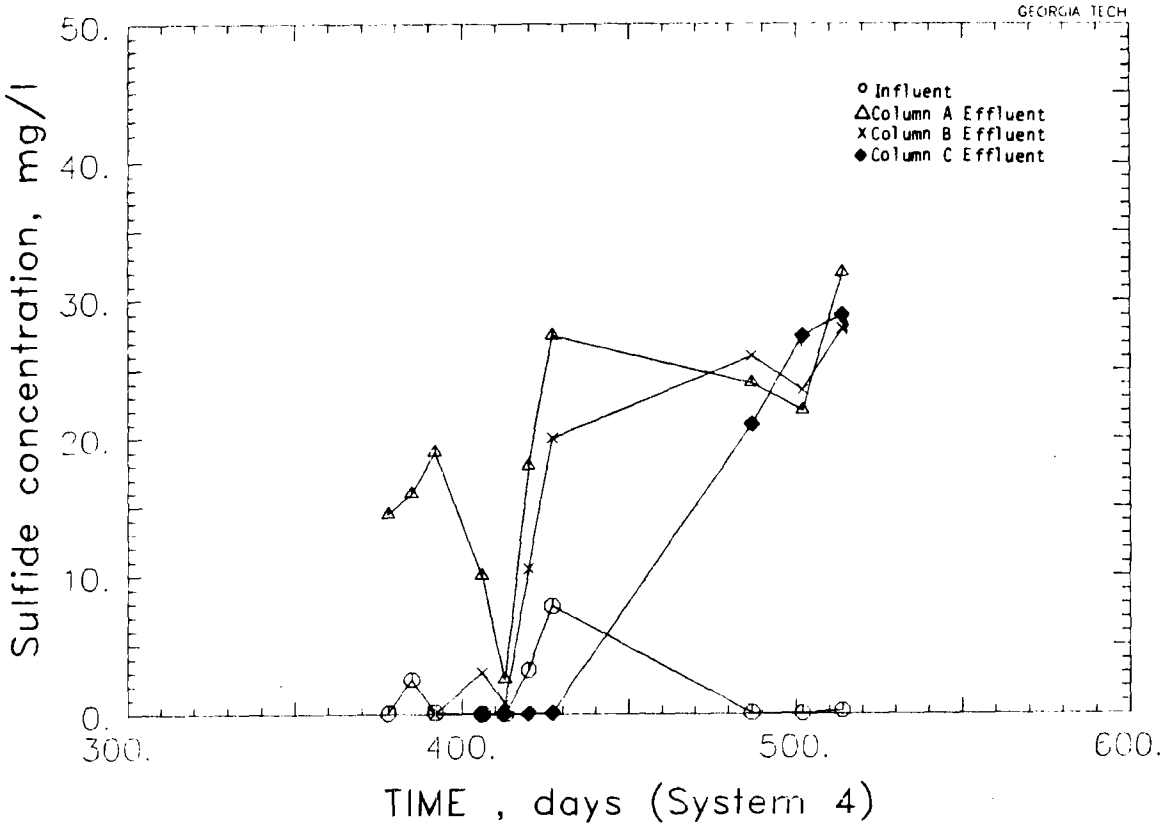


FIGURE 13

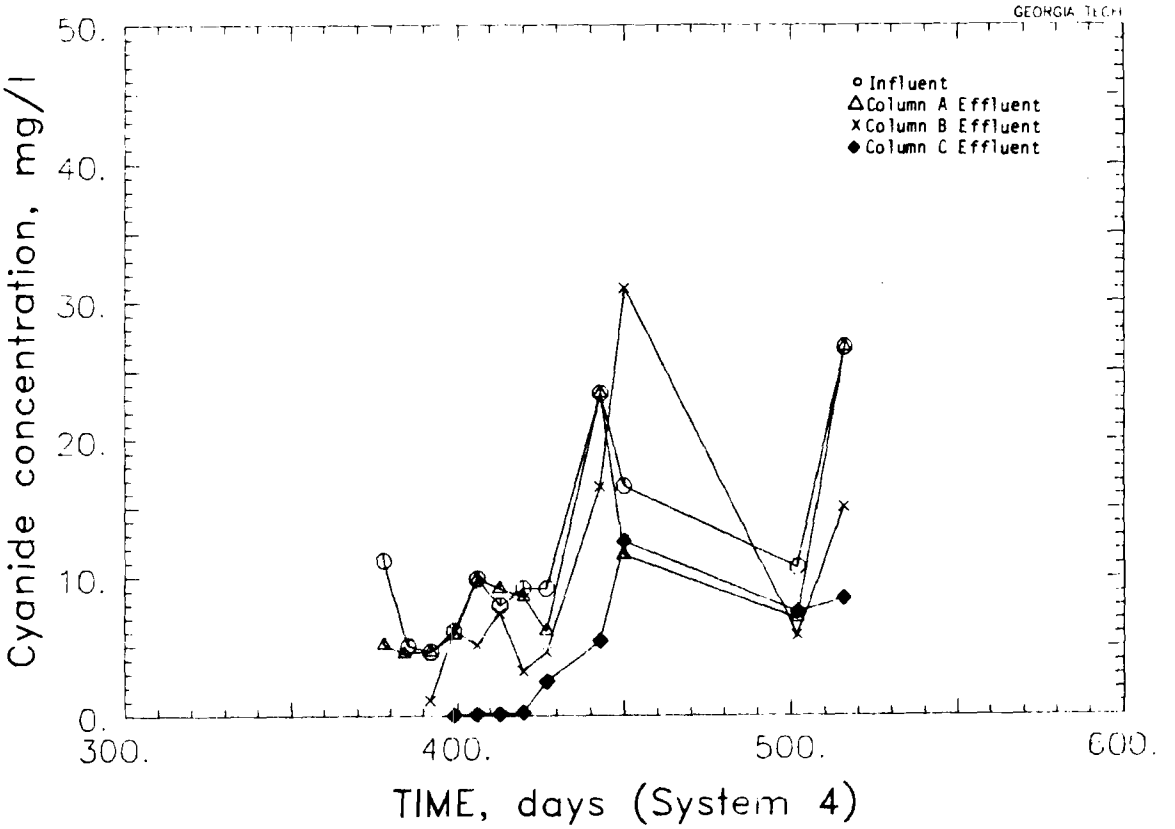


FIGURE 14

III. NITRIFICATION SYSTEM

1. Operation

Two nitrification systems are currently being operated under very similar conditions to treat the anaerobic effluent from Systems III and IV. The powdered activated carbon (PAC) addition to one of the nitrification systems (the one treating effluent from Anaerobic System III) was discontinued on day 456, the day that carbon addition/replacement was begun on Anaerobic System III. Since that time both nitrification systems have been operated as activated sludge systems at a solids retention time (SRT) of 30 days and a hydraulic retention time (HRT) of 30 hours.

2. Conversion Efficiencies

Both systems are operating quite well under the above conditions. Ranges of influent and effluent ammonia concentrations during this period are shown in Table I along with data for influent and effluent COD. Occasionally minor upsets of the system occur which is primarily attributable, at this time to fluctuation in pH due to consumption of the available alkalinity during the nitrification process.

Table 1

Influent-Effluent NH_3 and COD Values
Nitrification Systems

	NH_3, mg/l			COD, mg/l		
	Inf.	Eff.	Average Removal,%	Inf.	Eff.	Average Removal,%
Filter 3 Effluent	235-710	.8-106	97.0	539-2396	55-490	78
Filter 4 Effluent	510-760	.8-105	97.1	74-587	22-300	49

IV. DENITRIFICATION SYSTEMS

1. Operation

Two denitrification systems are being operated utilizing the nitrified effluent from Anaerobic System IV. This effluent is being used for its somewhat more uniform and consistent quality. Both systems have been acclimated and are being operated in a continuous flow mode utilizing methanol as a source of carbon. One system, a packed bed upflow system utilizing Beryl Saddles as a packing is currently operating at a hydraulic retention time of 36 hours and is removing greater than 95% of the influent NO_3^- . As soon as sufficient data has been collected at this HRT the loading to the system will be increased. The second system, a suspended growth slurry reactor, has just begun operation in a continuous flow mode. Sufficient data should be available for the next quarterly report to give a preliminary evaluation of the mode of treatment.

V. GC/MS Analysis of "Exhausted" Granular Activated Carbon and Stored Wastewater

1. Characterization of Wastewater

In order to quantitatively determine the major organic constituents, other than phenol and o-, m-, and p-cresol, present in the wastewater being utilized in the study, three samples of wastewater were analyzed for 21 other organic compounds which had previously been identified as being present in the wastewater. The data generated utilizing known standards and the wastewater samples have been placed in the GC-MS data system and can be used for a reference in processing future wastewater and carbon extracts. The three wastewater samples utilized were: 1) a sample from the original wastewater shipment, which had been stored frozen; 2) a sample from the original wastewater shipment which had been thawed and stored refrigerated for several months; and 3) a sample from the new wastewater shipment which had been stored frozen. A flow schematic of the extraction process utilized is shown in Figure 15. Five organic compounds (1,4-dichlorobenzene-d_4) napthalene-d_8, perylene-d_{12}, benzidine and phenol-d_6) were chosen as surrogates to monitor the analytical procedure. They were added to the raw wastewater sample at the 500 µg/L level prior to starting the solvent extraction process.

A summary of the results showing the total quantities of each compound found is given in Table 2. As can be seen from Table 2, there is apparently very little difference in the concentration of the major phenolic constituents between samples of wastewater currently being utilized in the study.

2. Extraction and Characterization of "Exhausted" Carbon.

Consideration of the possible inhibition of anaerobic systems by refractory/inhibitory constituents which had accumulated on the activated carbon has led to the extraction of the carbon and characterization of the extracts thereby obtained.

Activated carbon samples were obtained from Anaerobic Systems I, II and III. At the time of sampling, Anaerobic Systems I and II had ceased to produce methane

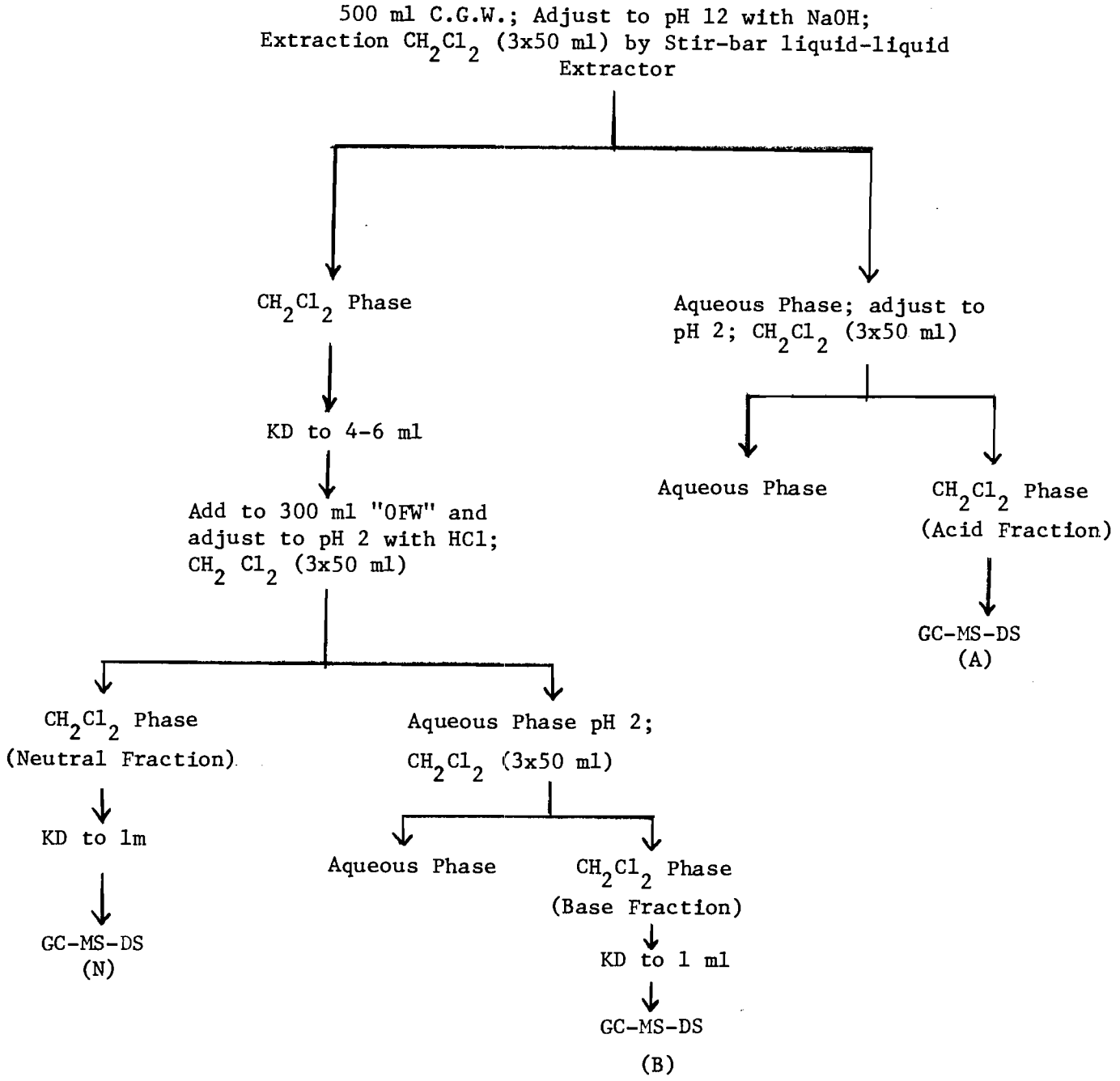


Figure 15. Schematic of Analytical Procedures for Solvent Extractable Organics in Coal Gasification Wastewater

TABLE 2.

Compound	Quantity Found, mg/l Original Frozen	Original Refrigerated	New Frozen
Pyridine	5.08	4.24	1.58
2-Picoline	4.55	2.98	.83
4-Picoline	7.48	4.31	1.04
Aniline	2.22	1.69	.47
Dimethylaniline	NF	NF	Trace
Benzonitrile	1.45	.11	.24
2-Methoxyphenol	209.2	129.5	87.9
2,6-Dimethylphenol	8.36	5.44	5.36
2-Ethylphenol	16.64	10.4	10.5
2,5-Dimethylphenol	152.6	98.1	108.2
2,4-Dimethylphenol		98.1	108.2
4-Ethylphenol	198.5	141.5	147.5
3,5-Dimethylphenol			
3-Ethylphenol	10.9	7.59	7.53
3,4-Dimethylphenol	34.0	23.4	22.3
4-Methoxyphenol	NF	1.02	.97
3-Methoxyphenol	.46	2.08	1.68
2,3,5-Trimethylphenol	4.58	2.27	1.88
Indole	1.89	2.64	2.55
2,6-Dimethoxyphenol	NF	NF	NF
3-Methylindole	.41	NF	.32

NF = Not Found

and the performance of System III had begun to decline. Carbon from Systems I and II had been stored frozen while the carbon from System III was obtained directly from the operating reactor. Therefore, the carbon was evaluated in terms of its moisture content and all results are reported on the basis of dry carbon weight.

Figure 16 outlines the extraction procedure utilized to obtain the extracts which were then analyzed utilizing GC-MS analysis.

Table 3 summarizes the data obtained from the above extraction procedure.

As can be seen from Table 3, the predominant species desorbed from the activated carbon are the cresols, phenol and the substituted alkyl phenols. It should be noted that the indoles, pyridines, picolines and methoxyphenols were not found in the carbon extracts or were present in very small amounts compared to their values in the raw wastewater. Either they are being removed by biodegradation or the extraction procedure does not desorb these from the carbon. The accumulation of the alkyl phenols on the activated carbon is indicative of their greater resistance to biodegradation and a greater capacity of the carbon for these particular compounds. As indicated in a previous report, the total cresol to phenol ratio increases approximately 20 fold from the influent value to the desorbed data values.

Table 3

Compound	Quantity Desorbed mg/g Dry Carbon		
	System 1	System 2	System 3
phenol	3.50	1.78	5.83
o-cresol	6.07	6.18	7.67
m-cresol, p-cresol	26.2	20.3	40.5
pyridine	.06	.12	.33
2-picoline, 4-picoline	.05	.28	.39
aniline	NF	NF	NF
2,6-dimethylanaline	NF	NF	NF
benzonitrile	.03	.02	.07
2-methoxyphenol	NF	NF	NF
2,6-dimethylphenol	.04	.10	.33
2-ethylphenol	.31	.42	.53
2,5-dimethylphenol, 2,4-dimethylphenol	2.11	3.24	6.73
4-ethylphenol	2.98	3.40	6.64
3,5-dimethylphenol, 3-ethylphenol	1.87	3.40	7.72
3,4-dimethylphenol	.51	.95	1.33
4-methyoxyphenol	NF	NF	NF
3-methoxyphenol	NF	NF	NF
2,3,5-trimethylphenol	.03	.05	.14
indole	NF	NF	NF
2,6-dimethoxyphenol	NF	NF	NF
3-methylindole	NF	NF	NF

NF - Not Found

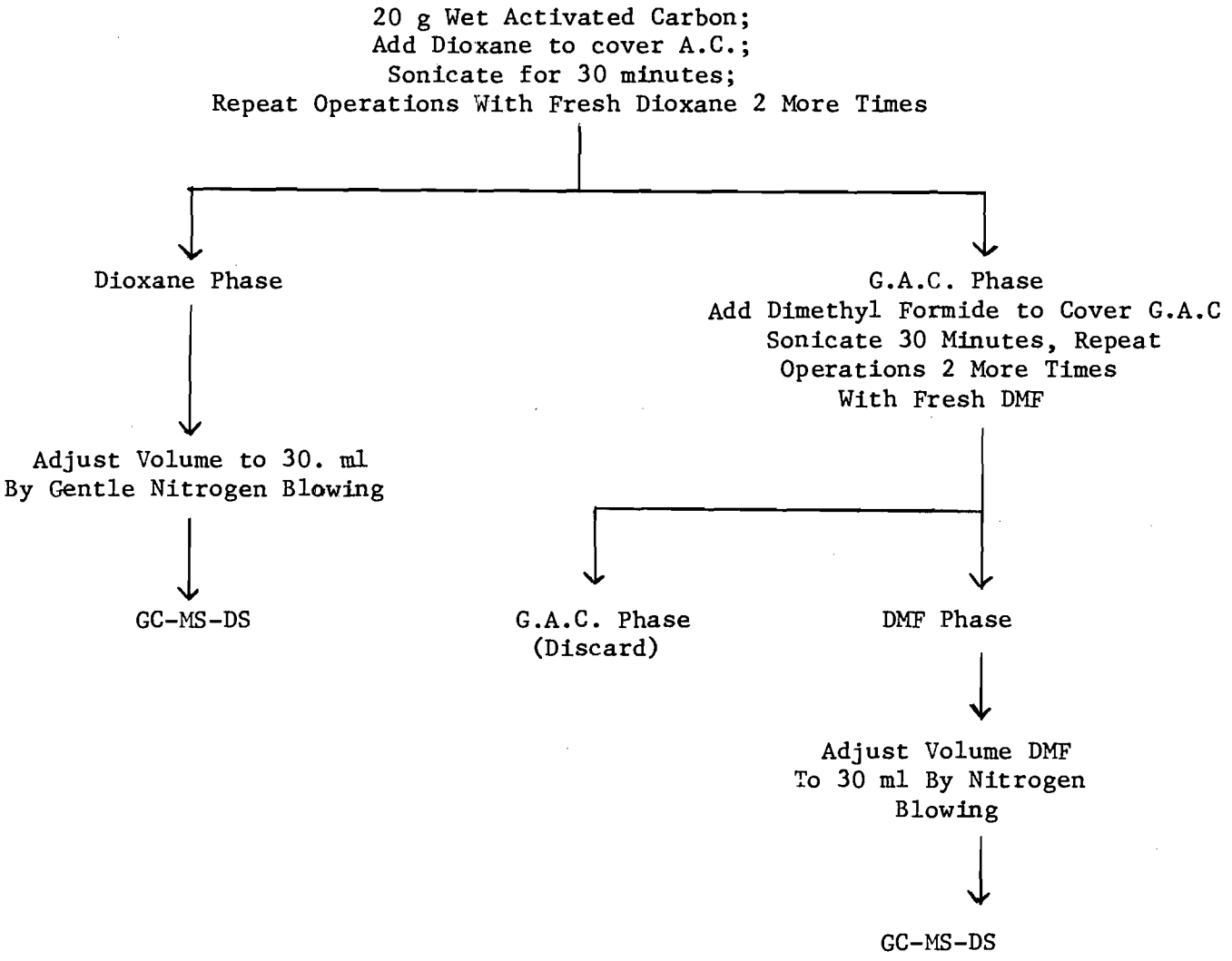


Figure 16. Flow Schematic of Analytical Procedures for Desorption of Organics from Granular Activated Carbon

VI. ULTRAFILTRATION - REVERSE OSMOSIS - STUDY

In view of the continued relatively high dilution of the raw wastewater for treatment in the anaerobic system (currently 10-12% raw wastewater) and the desirability of reusing as much water as possible in the overall gasification and treatment system a brief (one experimental run) study was carried out to ascertain the applicability of Reverse Osmosis and Ultrafiltration to the effluent of the wastewater treatment system. Nitrified effluent was used in the study because of its availability and overall chemical characteristics.

A sample (35 gallons) of nitrification system effluent was subjected to ultrafiltration using a HFJ-HFP-HFM series of membranes. The resulting ultrafiltration permeate was processed through a reverse osmosis unit. The results of the experiment are summarized in Table 4. As can be seen from Table 4, the ultrafiltration step had little effect in improving the water quality. However, reverse osmosis treatment of the ultrafiltration resulted in a permeate which was extremely low in total dissolved solids (TDS), color, inorganic carbon (TIC), and total organic carbon (TOC). Values for these parameters were 130 mg/l ~0 units, 5 mg/l and ~1 mg/l respectively. This water would be used either in the gasification process, as gas quench water, or dilution water for the anaerobic treatment system.

Table 4

Ultrafiltration - Reserse Osmosis Data

	Turbidity	Color	TDS, mg/l	TOC, mg/l	TIC, mg/l
UF - Feed	.4	169	3800	86	62
UF - Permeate	.3	246	4500	104	64
RO Feed*	-	239	4700	110	60
RO Feed**	-	1725	29500	550	370
RO Permeate	-	~0	130	1	5

*Initial Value
**Final Composited Sample

VII. FUTURE WORK

Carbon replacement on System III will be continued. At the present time, monitoring of cresol breakthrough will be utilized as the central parameter to determine the frequency of carbon replacement. In order to maintain sufficient biomass in the system, initial carbon replacement will be limited to 30 to 40% of the carbon in the system. System IV will be monitored for phenol, cresol breakthrough and a new column will be added to the system as soon as this occurs.

In order to ascertain if gas production can be increased in the biological systems, a trace metals solution will be added to the feed wastewater for an extended period.

Nitrification will continue with a pH controller, coupled to a pump for $NaHCO_3$ addition, utilized in the aeration basis to minimize upsets due to alkalinity consumptions. The nitrified effluent will continue to be used in the denitrification studies.

Denitrification will be continued and steady state data will be obtained for various loadings, and continuous flow operation using methanol as a carbon source.

Investigation into determining the specific compound(s) causing inhibition to the system will continue. Efforts will be focused on those compounds accumulated on the activated carbon. In addition, authentic samples of some hydantoins have been obtained and analytical procedures will be developed in order to monitor the concentrations of these species in the treatment system. Also, the fate of these compounds and their possible inhibition of the anaerobic system will be investigated when the analytical methodology has been completed.

Extraction studies of the "exhausted" carbon will continue in order to assure that the maximum number of compounds which are adsorbed on the carbon can quantitatively be desorbed and identified.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report #8
July 1983

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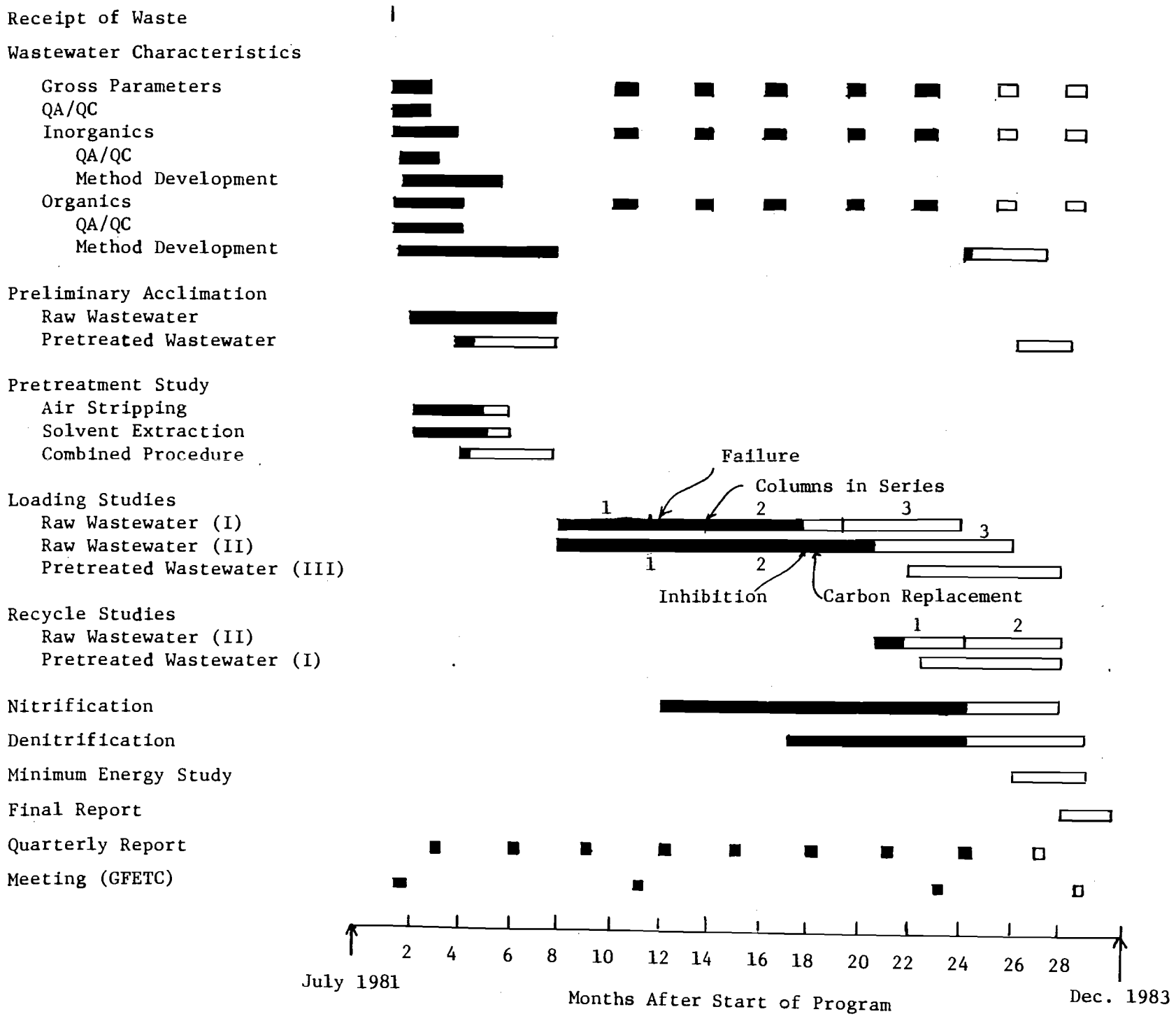
TABLE OF CONTENTS

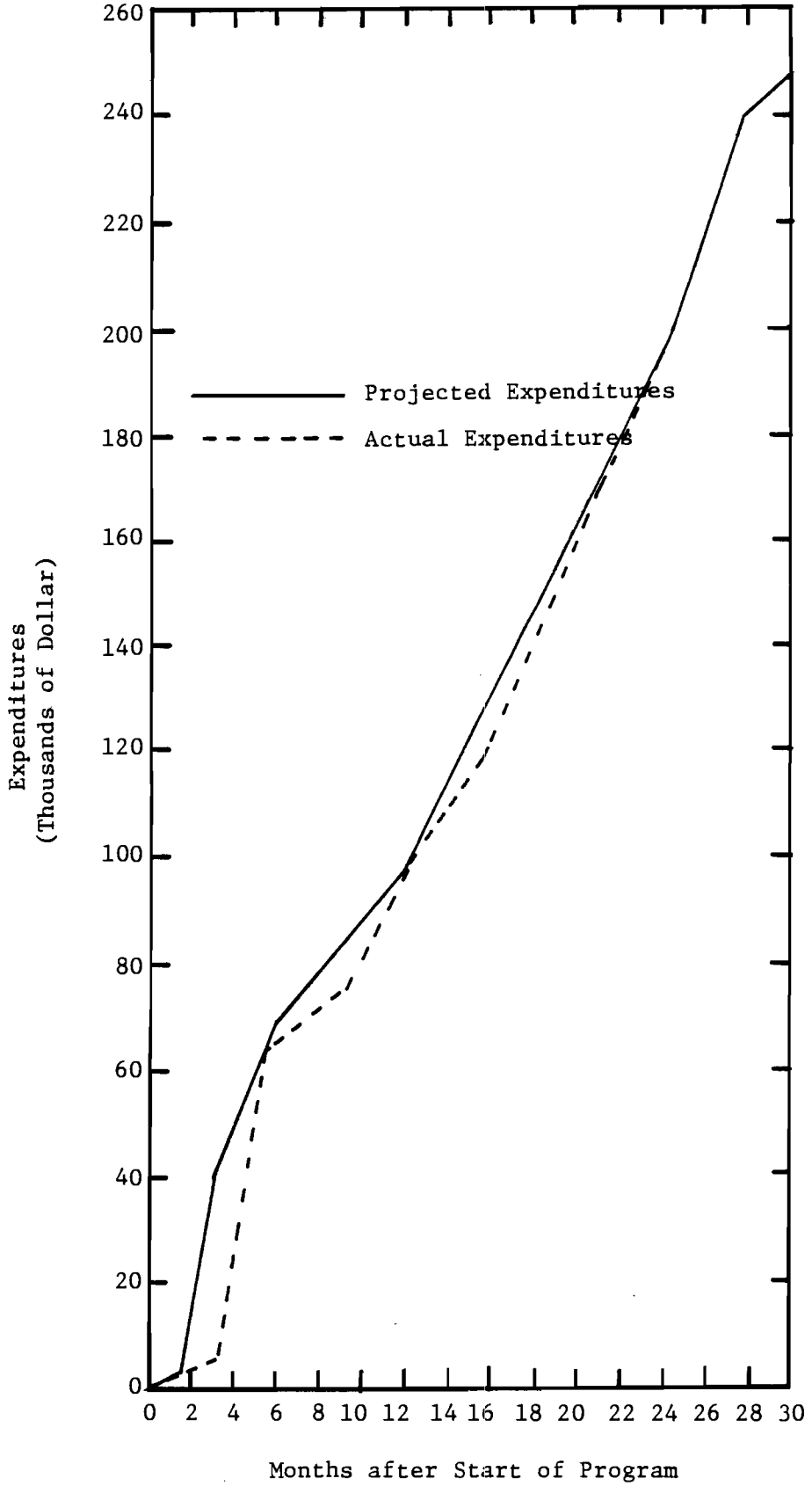
I. INTRODUCTION

This report summarizes the work performed during the period from April 1, 1983 through June 30, 1983 on the DOE research program on "Anaerobic Treatment of Gasifier Effluents" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward: 1) the operation of two anaerobic systems treating ~10% strength raw wastewater with activated carbon replacement occuring in one system, 2) the operation of two nitrifying systems treating the anaerobic effluent, and 3) the operation of both packed bed and suspended growth denitrifying systems for treating the effluent from the nitrifying systems. The progress of these efforts are depicted on the Gannt Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.

Task 2

Schedule For Research Program





Projected Expenditures for DOE Contract
No. DE-AC18-81FC10297

Figure 2.

II. ANAEROBIC TREATMENT SYSTEMS

A. System III

1. Operation

System III has now been operating an additional 90 days (total operation 540 days) on ~10% raw wastewater at a flow of 10 ml/min. The carbon replacement scheme begun last quarter has been continued with varied success as shown by removal efficiencies and gas production rates in the following figures and discussions.

Table 1 list the carbon replacements and other operating changes associated with System III operation.

2. Removal Efficiencies

Figures 3, 4, 5, and 6 (total cresols, phenol, COD and TOC respectively) show each time a fraction of the carbon was replaced there was an immediate decrease in the effluent values for each of the above parameters resulting in greater removal efficiencies and better overall performance of the system. However, as can be seen in Figures 7 and 8 (Gas Composition and Gas Production respectively) there was no marked increase in gas production as during previous carbon addition. In fact gas production decreased markedly and the percent CH_4 in the gas phase also decreased. On day 560 the large increase in gas production was due to an air leak in the recycle pump. This leak was repaired and gas production and CH_4 content increased slightly. On day 591 a temperature controller failure allowed the system temperature to reach 55°C. In order to obtain better gas production the Raschig Ring column was seeded with 2.5 liters of sludge supernatant on day 592 and day 599 the contents of the activated carbon column were transferred to a new column which had been modified to facilitate the removal and addition of granular activated carbon. Since that time there has been an increase in the CH_4 content of the gas phase and a slight

TABLE 1

SYSTEM 3

Day Number	Comment
456	Add 1 liter of carbon.
488	Add 2 liters of carbon, and removed 3 liters of carbon.
528	Added 4 liters of carbon, and removed 4 liters of carbon.
574	Added 1 liter of carbon, and removed 1 liter of carbon.
591	Temp of AC column reached 55C, recirculation pump shut down for 2 hours.
591	Injected 18g of glucose. Gas was produced.
592	Supernatant of domestic wastewater sludge fed to the RR column (approx. 2.5L).
592	Added 3 liters of carbon, and removed 2 liters of carbon.
593	New feed, TOC = 860 mg/1.
595	RR column produced 1.2 L of gas, 1% methane. Gas system checked and no leaks found.
599	Contents of AC column transferred to modified column with inlet and outlet ports for carbon cycling. One liter of carbon removed from AC column.
601	Increased influent flow rate from 6 to 8 ml/min.
612	Feed pump replaced.
614	New feed tank, TOC = 790 mg/1.
620	Added 2 liters of carbon, removed 1 liter of carbon.
620	New feed tank, TOC = 520 mg/L.
621	Feed tank TOC adjusted to 840 mg/L.
623	Domestic wastewater sludge (approx. 4L) added to RR column

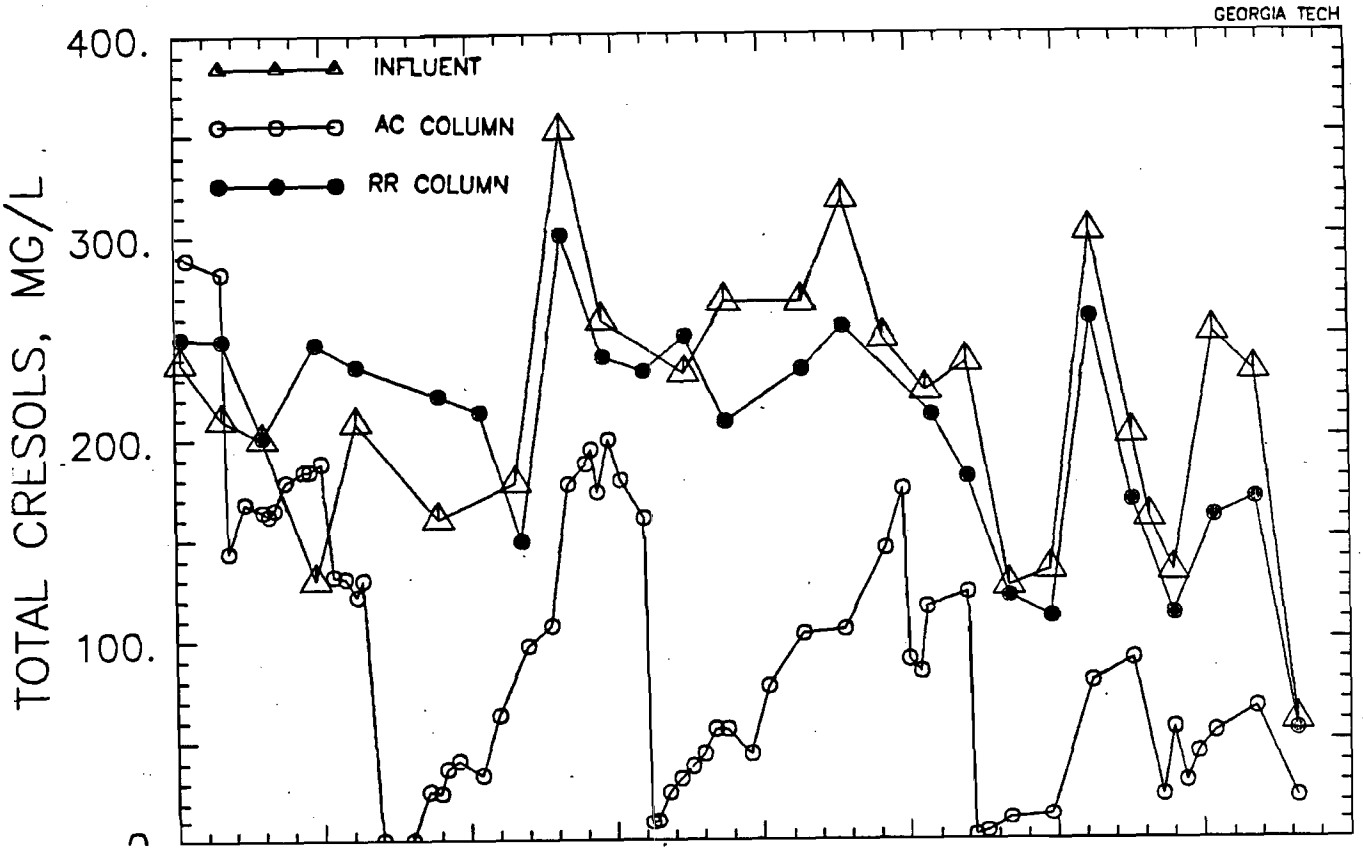


Figure 3

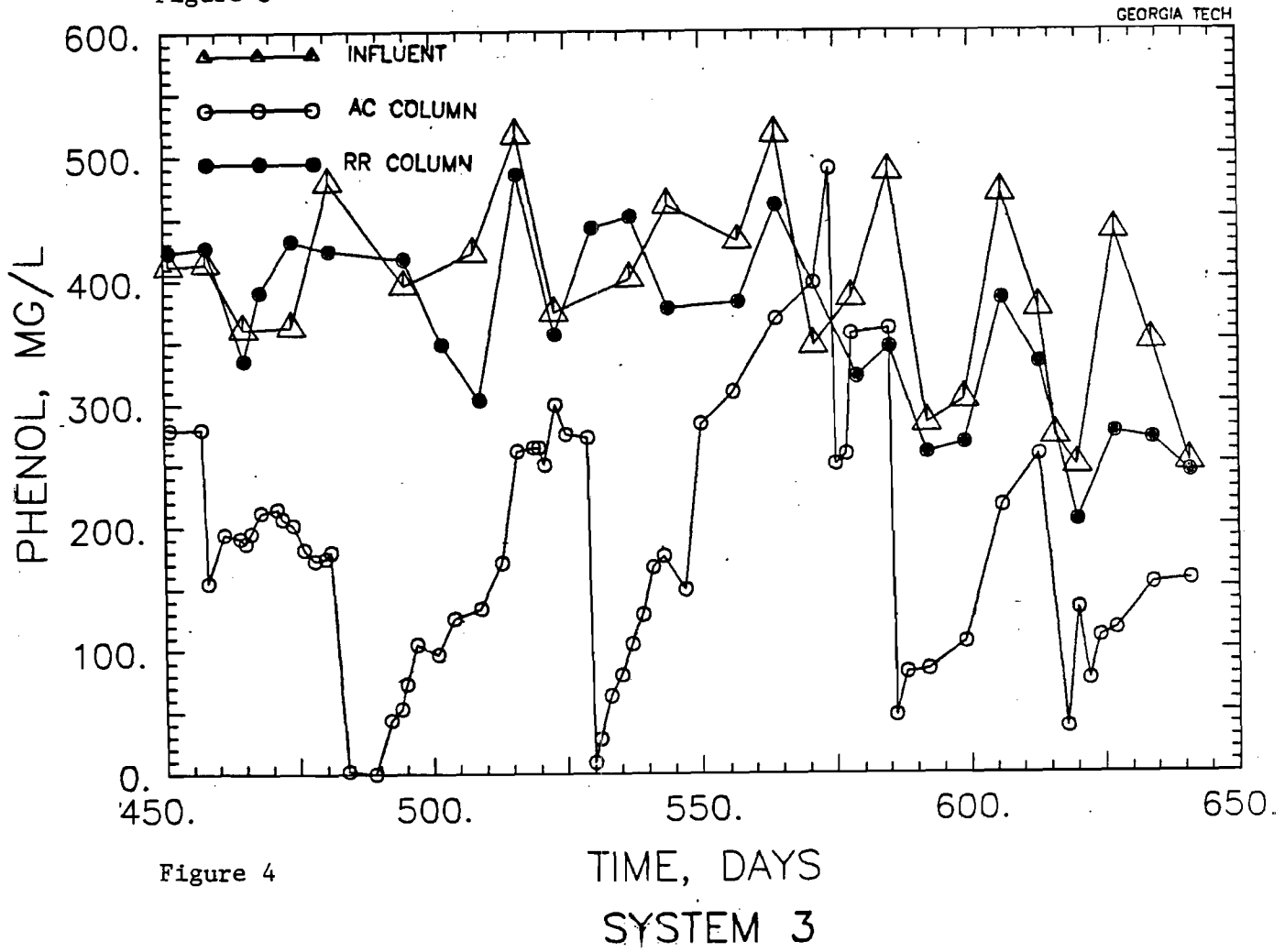


Figure 4

SYSTEM 3

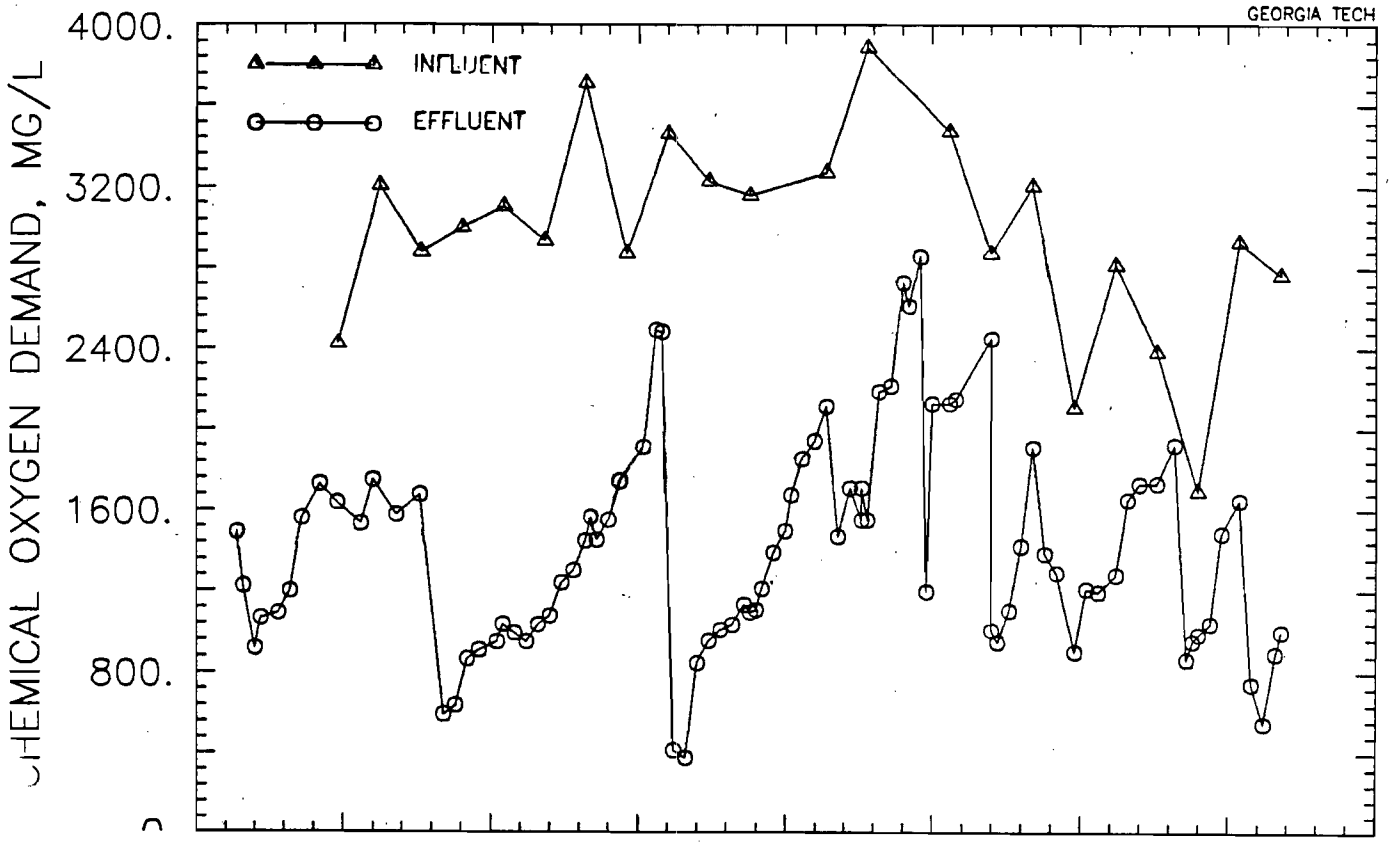


Figure 5

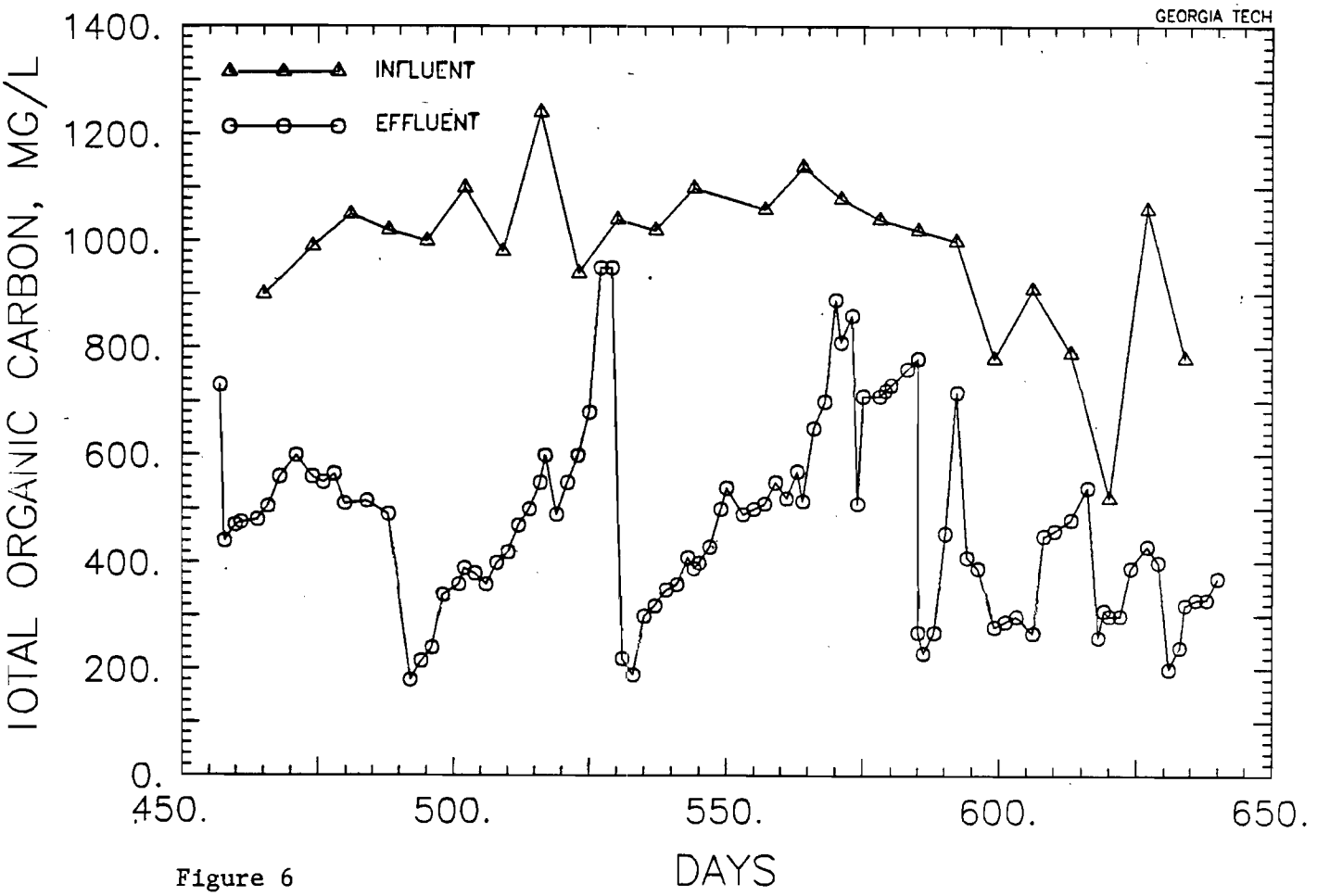


Figure 6

SYSTEM 3

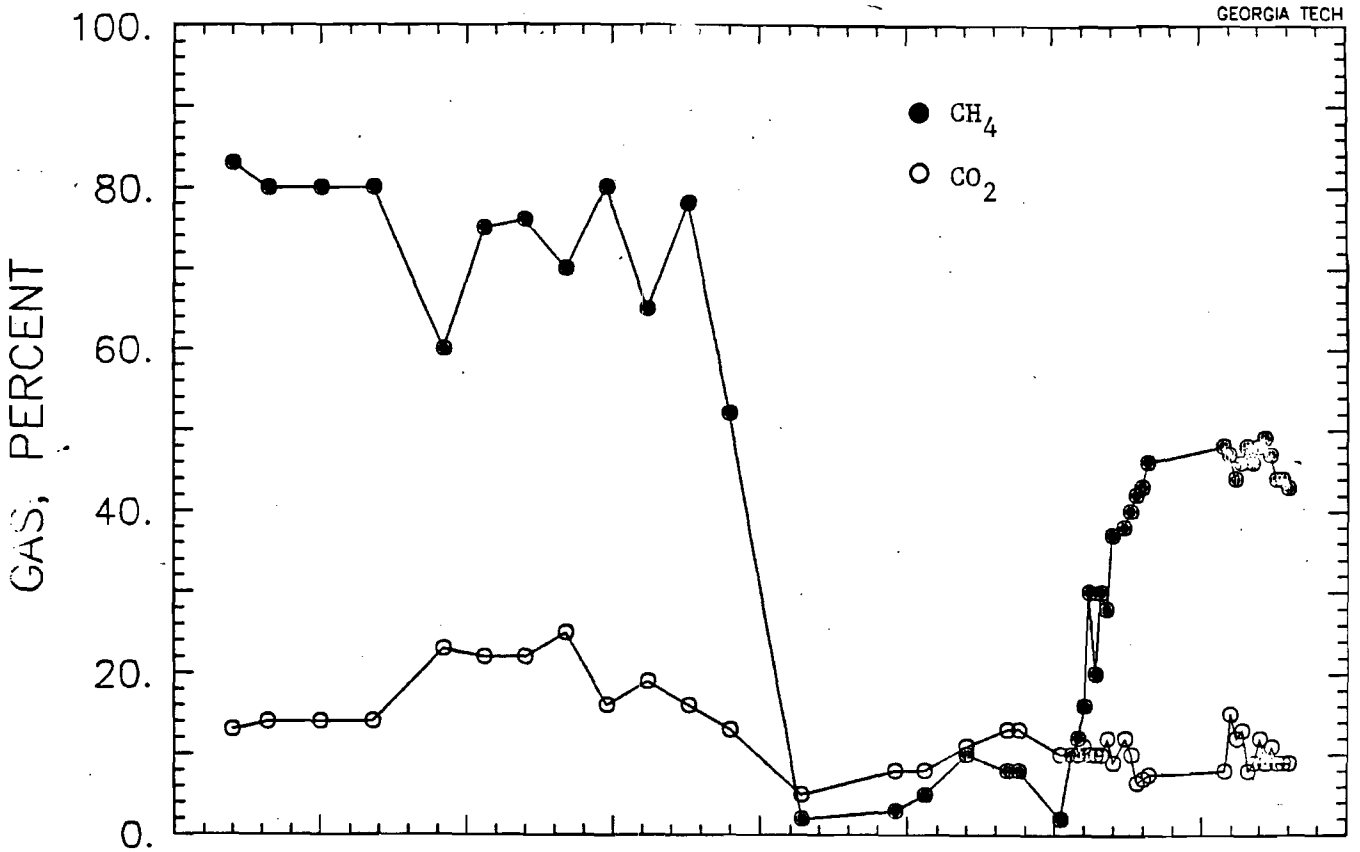


Figure 7

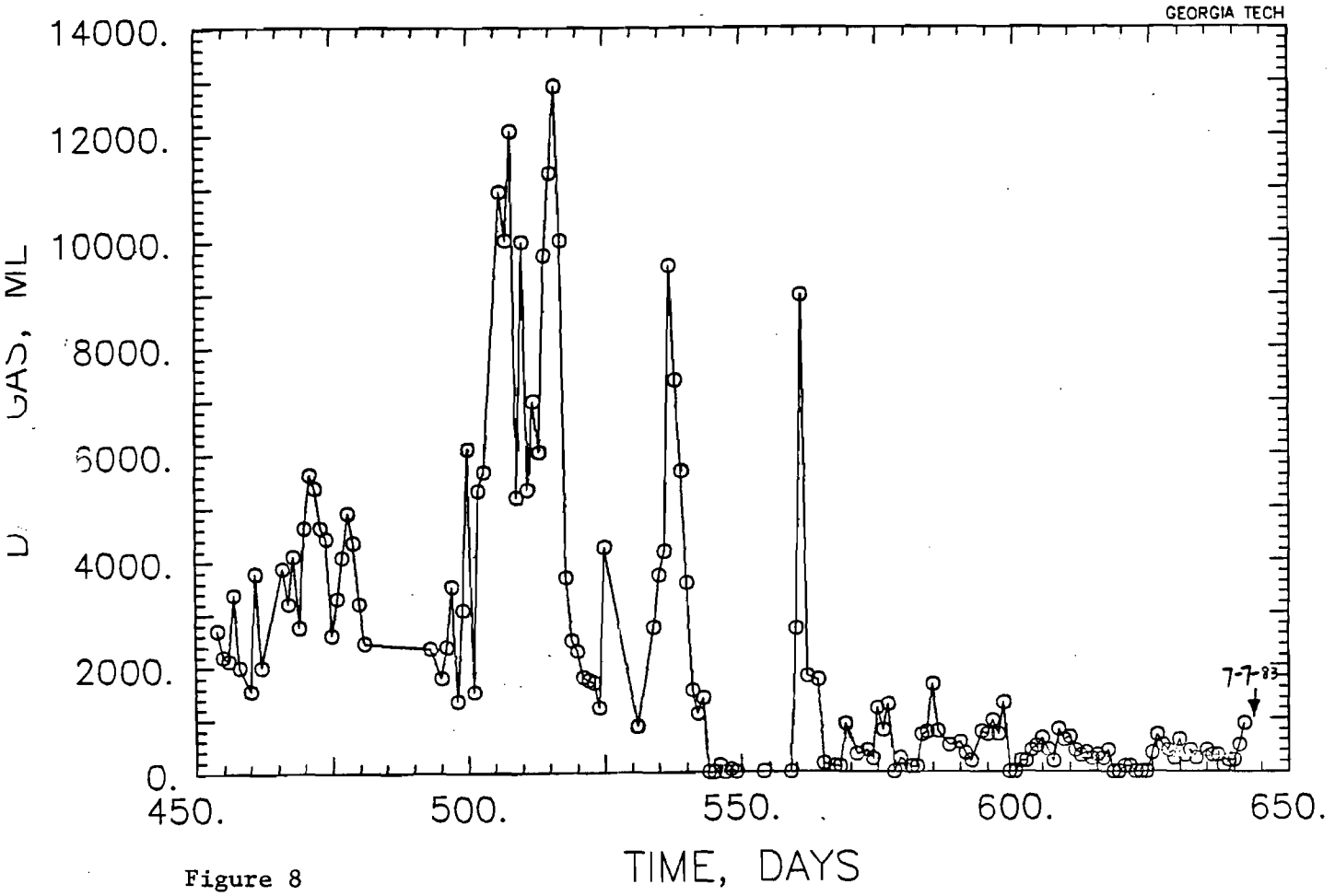


Figure 8

SYSTEM 3

increase in gas production. Steps have been initiated to increase the gas production rate by continuing the activated carbon replacement to reduce the concentration of inhibitory compounds and by seeding the column with effluent from an active phenol degrading anaerobic system.

Removal efficiencies in terms of COD and TOC remain in the 50 to 60% range, while phenol removal ranges from 40 to 95% and cresol removals range from 70 to 99% depending on the carbon replacement schedule.

B. System IV

1. Operation

System IV continued to show breakthrough of phenol in column A, B, and C with little or no gas production from column B or C. It was therefore decided to replace columns B and C with a single fresh activated carbon column in order to establish a viable gas producing system. Therefore on day 587 a new column (4D) replaced columns 4B and 4C in System IV. As can be seen in Figure 9 and 10, gas production from System IV remains relatively low while the CH_4 content is still in the 60% range. Column 4D is being seeded with effluent from an active phenol degrading anaerobic system in order to establish a viable gas producing microbiological population.

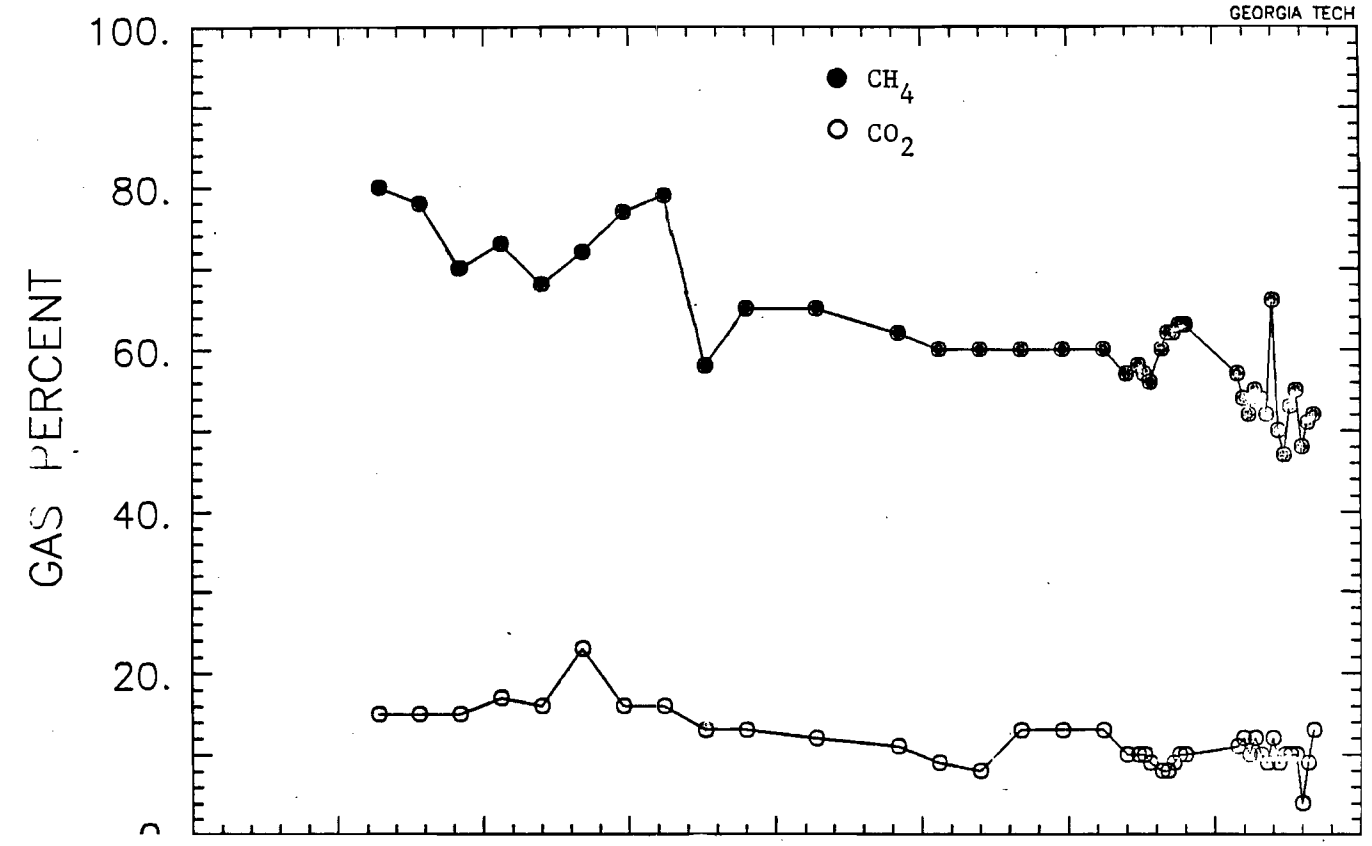


Figure 9

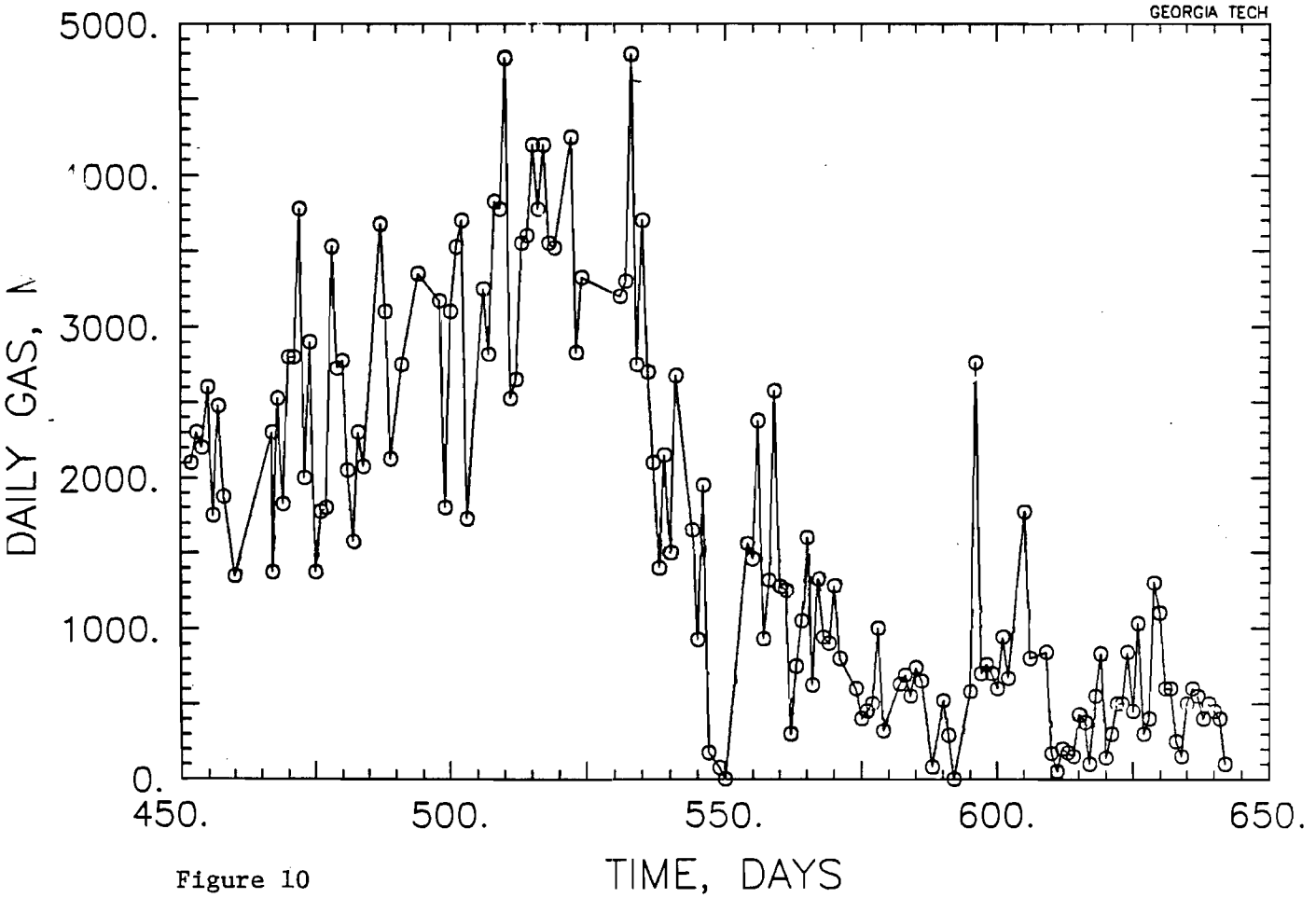


Figure 10

SYSTEM 4

III. NITRIFICATION SYSTEMS

1. Operation and Performance

Both nitrification systems are operating extremely well. They are being operated at solids retention times of 30 days and hydraulic retention time of 30 hours. Conversion of NH_3-N to NO_3^--N is essentially complete with very little NO_2^--N appearing in the effluent. In addition COD removals are quite good with average removals in the 70 to 80% range.

IV. DENITRIFICATION

1. Operation

Denitrification studies with treated coal gasification wastes are continuing. Two continuous-flow reactors are being operated to treat effluent samples from an aerobic activated-sludge system receiving anaerobically treated coal-gasification waste.

An upflow, packed-bed (beryl-saddles) anoxic reactor is being used to examine the feasibility of denitrification of the treated coal-gasification waste. The reactor is being operated at a feed rate of 0.7g NO_3-N/L·d (44 lb NO_3^--N/1000 ft^3·d). Excess methanol has been added to assure complete denitrification which has been effectively achieved. The methanol-carbon requirements are approximately 1 g MeOH-C/g·NO_3^--N or 4.0 g COD/g·NO_3^--N. Solvent-extracted, ammonia-stripped, coal-gasification waste has also been examined as a carbon source. The packed-tower reactor has been acclimated on a staged basis to the waste with no indication of inhibition. At present, 30 percent of the influent carbon is attributable to the pretreated waste while 70 percent is methanol. Within the next 10-day period full conversion to the pretreated coal-gasification waste will be achieved. A subsequent phase will be focused on evaluation of the use of raw coal-gasification waste as the sole carbon source.

A suspended-growth denitrification reactor with biomass recycle is also being used to examine denitrification. An acclimated culture has been developed, without intentional biomass wastage, at a cell residence time of 60 days with excellent NO_3^--N removal. The reactor is now being acclimated at a cell residence time of 30 days. Subsequent studies are to include acclimation at cell residence times of 20 and 10 days, as well as an investigation of the use of alternative carbon sources, i.e., raw and pretreated coal gasification wastes.

V. FUTURE WORK

Carbon replacement on System III will be continued. Monitoring of cresols will still be used as the central parameter in order to furnish quality effluent for the operation after nitrification and denitrification systems.

Nitrification will continue as it is currently being operated in order to furnish effluent for the denitrification system. The denitrification systems will be fed increasing concentrations of pretreated wastewater, while the methanol concentration in the feed is decreased in order to ascertain whether or not pretreated wastewater can be used as a carbon source for the denitrification process.

Development of analytical methods for the routine monitoring of hydantoins will continue in order to monitor the fate of these compounds in the process streams.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

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September 1983

by

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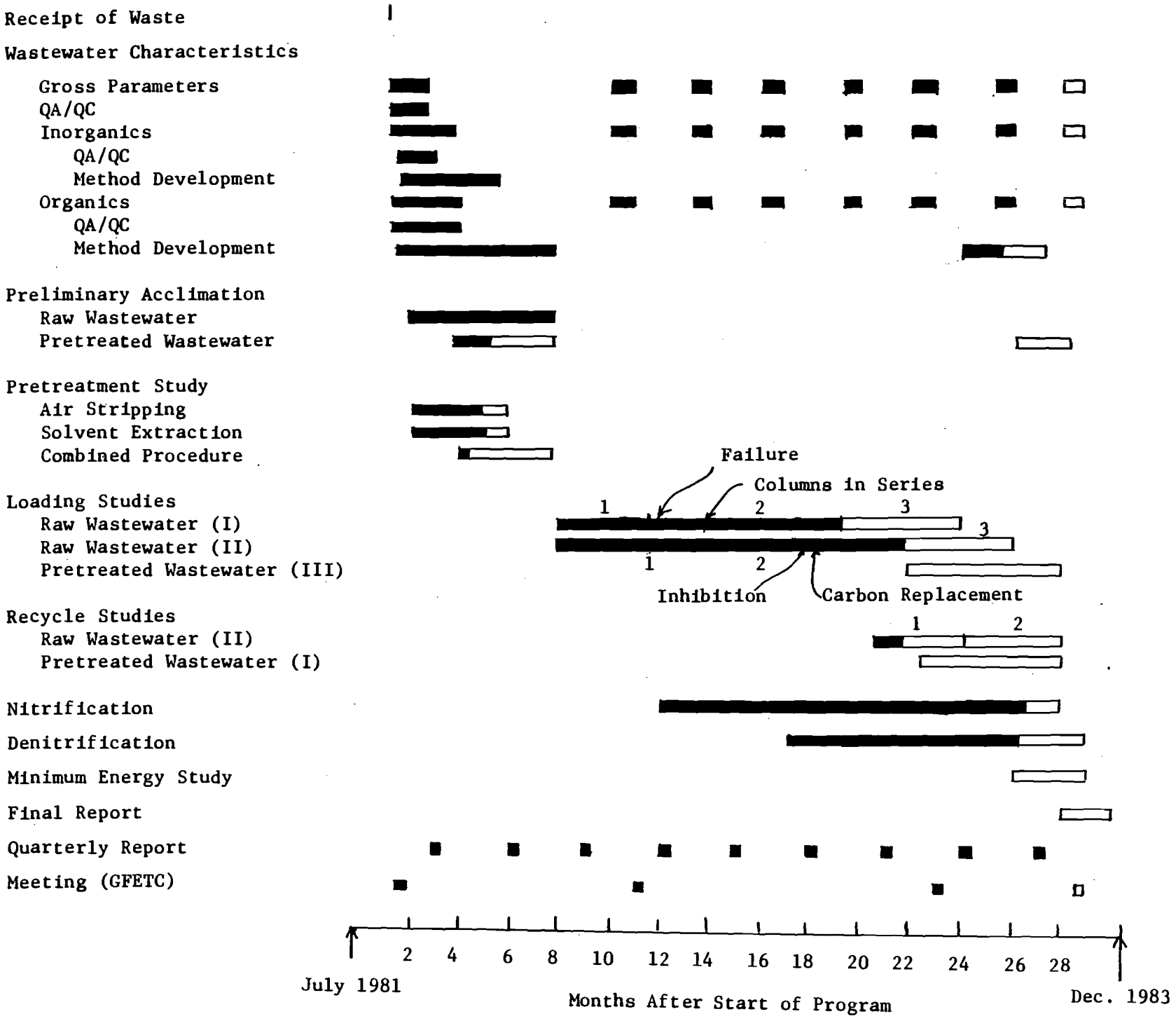
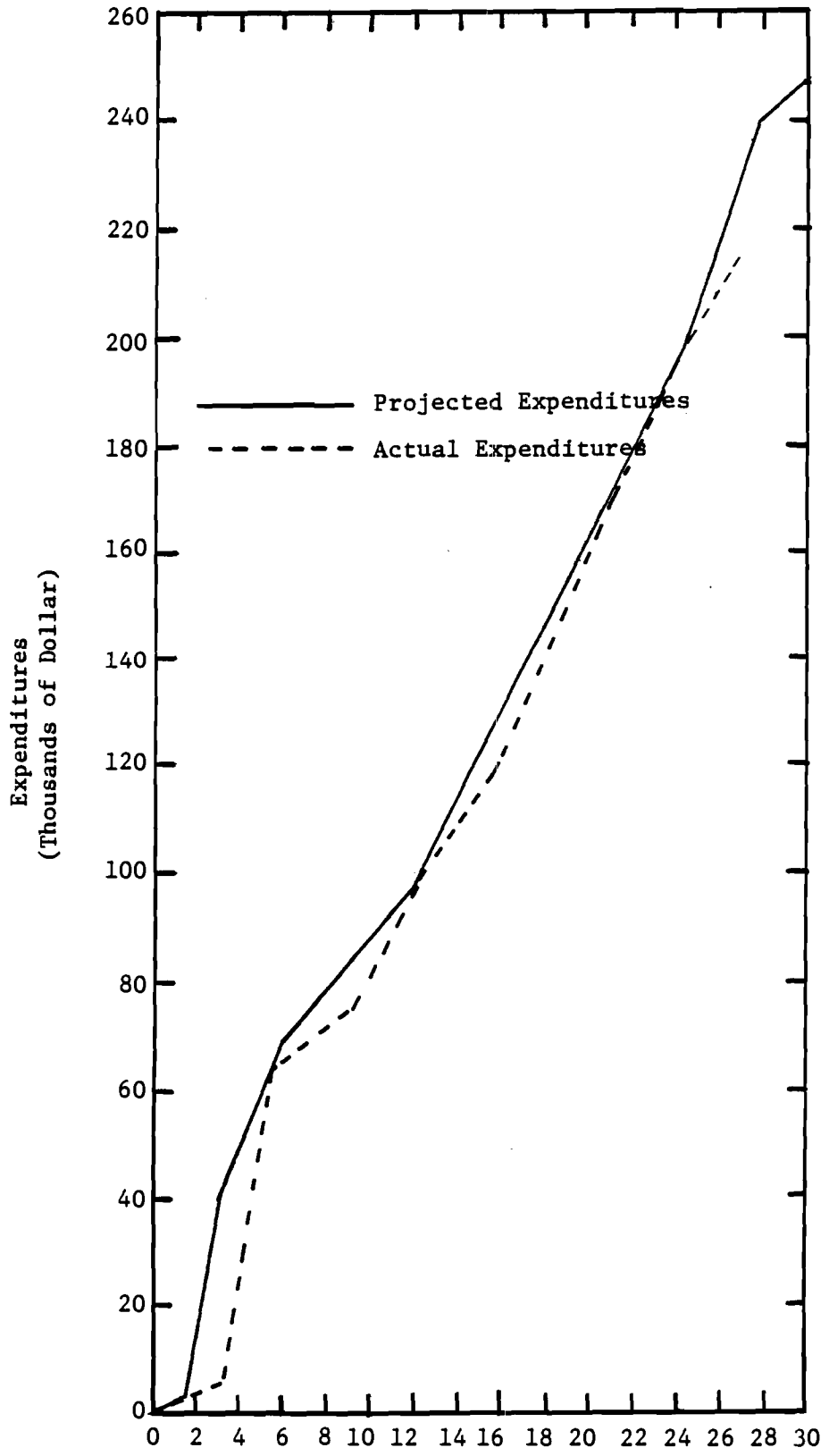
I. INTRODUCTION

This report summarizes the work performed during the period from July 1, 1983 through September 30, 1983 (Day 636-728) on the DOE research program on "Anaerobic Treatment of Gasifier Effluent" (Contract No. DE-AC18-81FC10297). The major efforts have been directed toward: 1) the operation of two anaerobic systems treating ~10% strength raw wastewater with activated carbon replacement occurring in both systems, 2) the operation of a nitrifying system treating the anaerobic effluent, and 3) the operation of both packed bed and suspended growth denitrifying systems for treating the effluent from the nitrifying system. The progress of these efforts are depicted on the Gannt Chart (Figure 1) along with project expenditures for the above contract (Figure 2) and are presented in detail in the following section.

Schedule For Research Program



Task 2



Projected Expenditures for DOE Contract
No. DE-AC18-81FC10297

Figure 2.

II. ANAEROBIC TREATMENT SYSTEMS

A. System III

1. Operation

System III has now been operated an additional 90 days (total operation 540 days) on ~10% raw wastewater at a flow rate of 10 ml/min. Partial carbon replacement has been utilized for the last 270 days of operation with improved performance of the system.

2. Removal Efficiencies

Removal efficiencies vary with the carbon replacement schedule due to the greater adsorption capacity of the fresh carbon. Best removals occur immediately following carbon replacement and then decrease as the carbon becomes saturated with organic matter.

Effluent COD values range from a low of approximately 200 mg/L to a high of 1,100 mg/L when the system received a temporary shock load. Average COD removal is approximately 75%.

Effluent TOC values are less than 100 mg/L immediately following carbon addition and range from 150 to 250 mg/L. Influent TOC values average 700 mg/L for this period resulting in an average removal of 80%.

Phenol and total cresols in the effluent are less than 100 and 50 mg/L respectively while influent values are approximately 300 mg/L for phenol and 200 mg/L for cresols.

3. Gas Production

During this reporting period gas production has steadily increased from a low of less than 1 L/day (Day 636) to a maximum of 14 L/day on Day 728. Gas composition has varied with the methane content increasing from a low of 10% on Day 645 to 68% on Day 728.

B. System IV

1. Operation

System IV is being operated under the same conditions as System III and receiving identical feed.

2. Removal Efficiencies

Removal efficiencies, in terms of phenol, cresols, TOC and COD parallel those in System III.

3. Gas Production

Gas production in System IV still lags behine that of System III. Column 4A has consistently produced approximately 1 L/day during the reporting period while the gas production from column 4D has increased from less than 1 L/day on Day 636 to a maximum of 5 L/day on Day 728. Gas composition has varied during the reporting period. Initially, (Day 636) the gas was 55% methane which decreased to 20% methane (Day 645) and then rapidly increased to 74% methane (Day 66) for the remainder of the period.

III. NITRIFICATION SYSTEM

1. Operation and Performances

No changes in the operation of the nitrification system has occurred. Complete nitrification of the anaerobic effluent is still occurring with no apparent inhibition or other problems.

IV. DENITRIFICATION

1. Operation and Performance

The upflow, packed-bed anoxic reactor has been acclimated to 50% and 100% pretreated coal gasification wastewater as the carbon source for denitrification. When using either the diluted or the full strength pretreated wastewater as the carbon source incomplete denitrification occurred. When pretreated wastewater and methanol are simultaneously used as a carbon source complete denitrification occurs. The results indicates that a considerable fraction of the carbon contained in the pretreated wastewater is unavailable for denitirfication. However, there is no apparent inhibition to the denitrification process attributable to the refractory compounds in the pretreated wastewater.

The suspended growth denitrification reactor has been successfully operated at a cell residence time of 15 to 25 days with complete nitrate removal. Hydraulic retention time is approximately 24 to 30 hours.

V. FUTURE WORK

Partial carbon replacement will continue and will be practiced on a more frequent basis on both Systems III and IV. Approximately 10% of the carbon in each column will be replaced every 10 to 15 days. Along with the more frequent carbon replacement, loadings to the system will be increased. This will be accomplished by first increasing the hydraulic retention time in the system and then increasing, in a stepwise fashion, the concentration of the wastewater in the feed to the system until the original mass loading is attained. Further increases in feed wastewater concentrations will then be carried out to ascertain the effect of increased loading to the anaerobic systems.

The use of raw wastewater as a carbon source for denitrification will be evaluated.

Work will be initiated on an investigation of the fate of hydantoins in the anaerobic system along with the determination of the concentration at which specific wastewater components cause inhibition of the anaerobic process. Solvent regeneration of activated carbon removed from the anaerobic system will also be studied.

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Quarterly Report
December 1984

by

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I. INTRODUCTION

This report summarizes the work performed during the period from July 1, 1984 through December 31, 1984 (Day 1001 to Day 1186) on the DOE research program on "Anaerobic Treatment of Gasifier Effluent - Inhibition and Fate of Hydantoin Studies" (Contract No. DE-AC18-81FC10297). The major efforts have been directed towards: 1) serum bottle inhibition studies of selected wastewater constituents, 2) studies of the adsorption of hydantoins on granular activated carbon, 3) initiation of a continuous flow granular activated carbon filter for treating pretreated wastewaters and 4) initiation of an adsorption-regeneration study utilizing pretreated wastewater.

II. ANAEROBIC TREATMENT SYSTEM

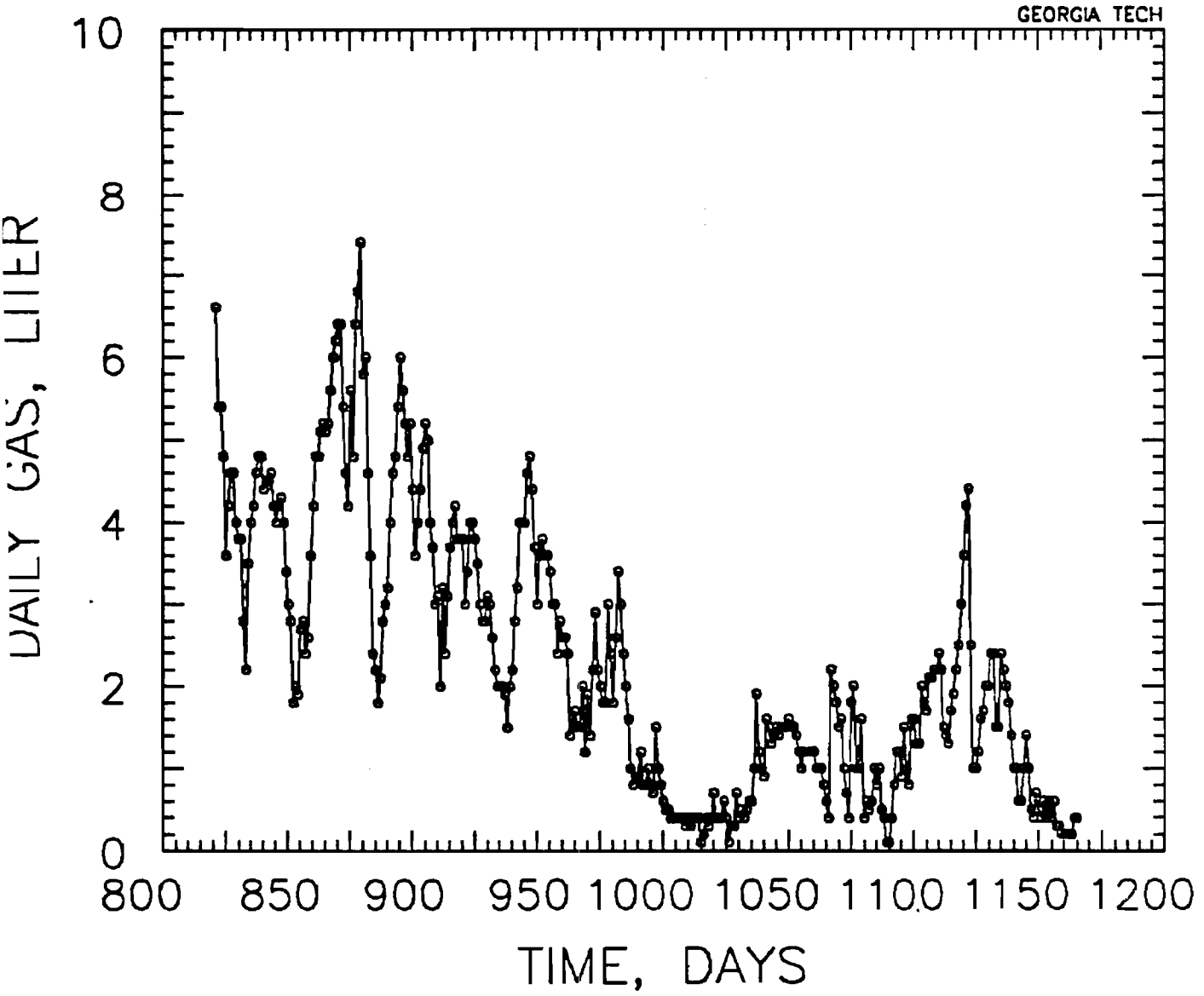
A. System III - Continuous Flow Studies

System III was operated with partial carbon replacement on dilute raw coal gasification effluent until December 10 (Day 1165). Up to Day 1165 performance was somewhat erratic depending upon the quantity and scheduling of the granular activated carbon replacement.

Gas production (Figure 1) varied from a few hundred milliliters per day up to a maximum of 5 L/day. Gas composition was constant at approximately 28% CO_2 and 70% methane (Figure 2).

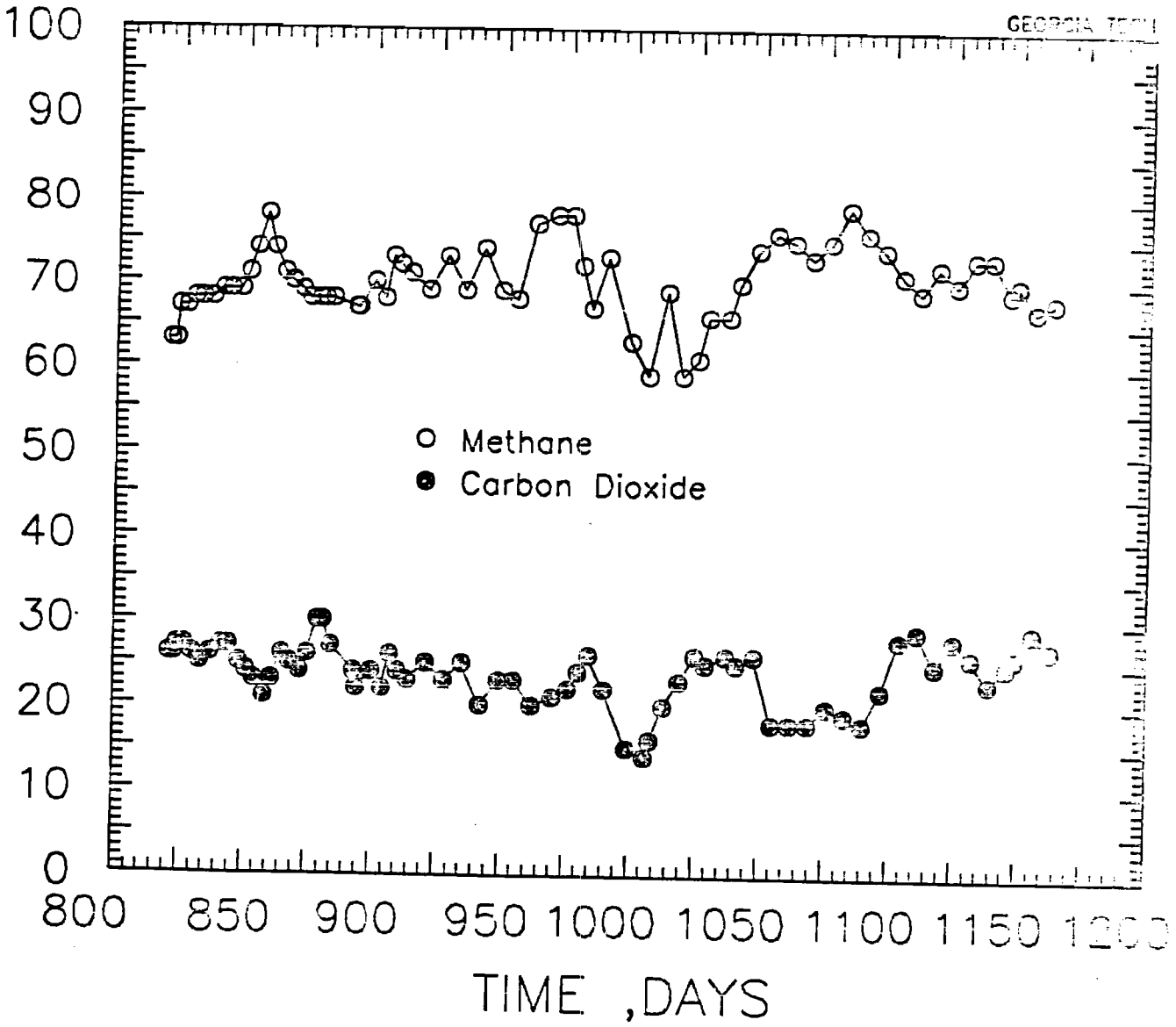
Effluent phenol, TOC and cresol values remained relatively constant and low (Figures 3, 4 and 5). However, effluent COD values have shown a small but relatively steady increase during the period (Figure 6). This might be attributable to displacement of a more highly reduced organic compound from the granular activated carbon by a less reduced species.

On Day 1165 the influent to System III was changed from dilute raw coal gasification effluent to dilute pretreated wastewater. The initial TOC of the dilute pretreated wastewater was 200 mg/L (approximately 15% pretreated wastewater). Shortly after changing the influent source mechanical problems were encountered with the recycle system and fluidization of the carbon bed was lost. These problems have been corrected and the system is now functioning properly. Feed flow rate is 2 mL/min and the system is being allowed to acclimate to an influent containing predominantly hydantoins. Gas production has not begun. However, TOC removal is approximately 50%.



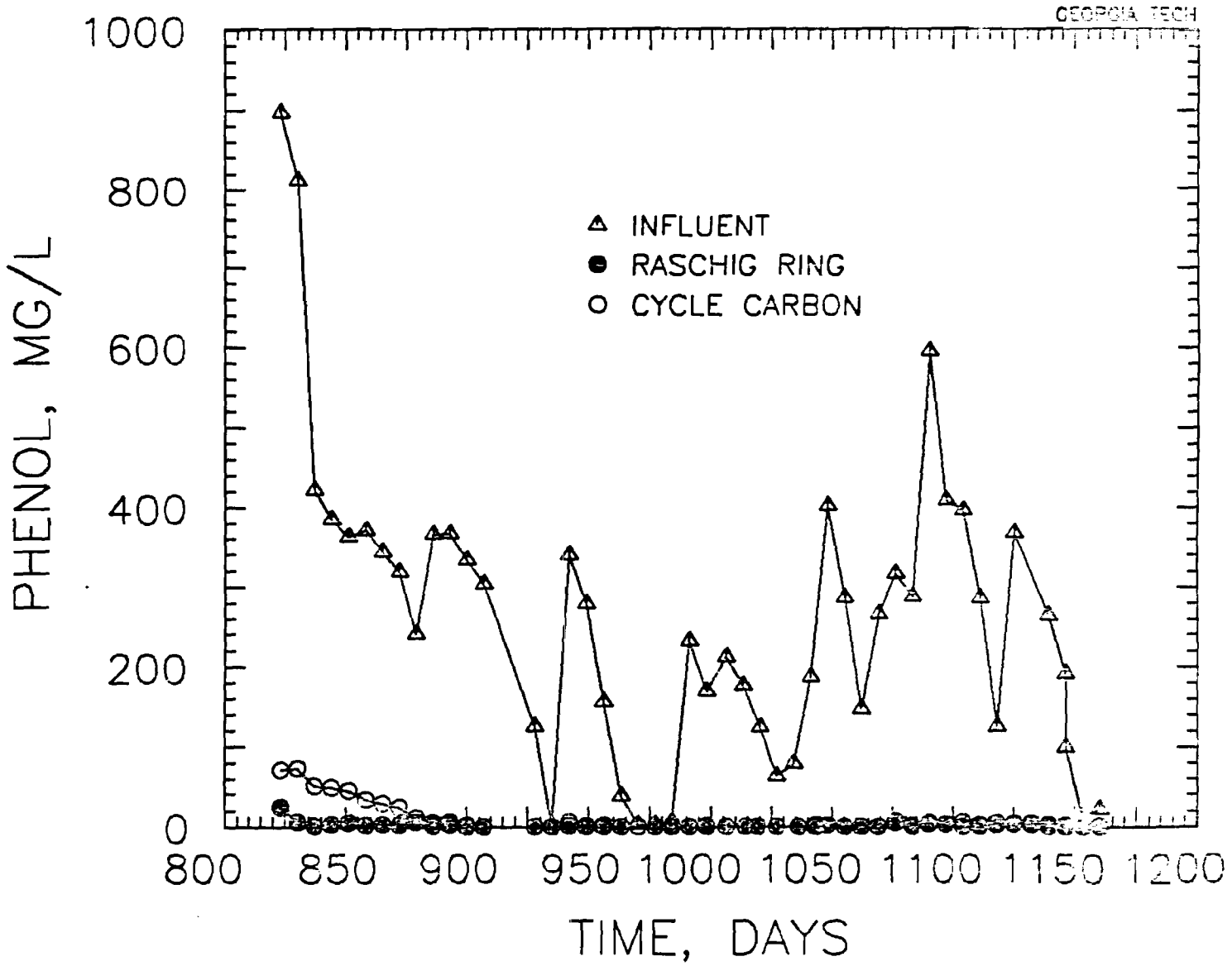
Gas Production of Column 3A

Figure 1



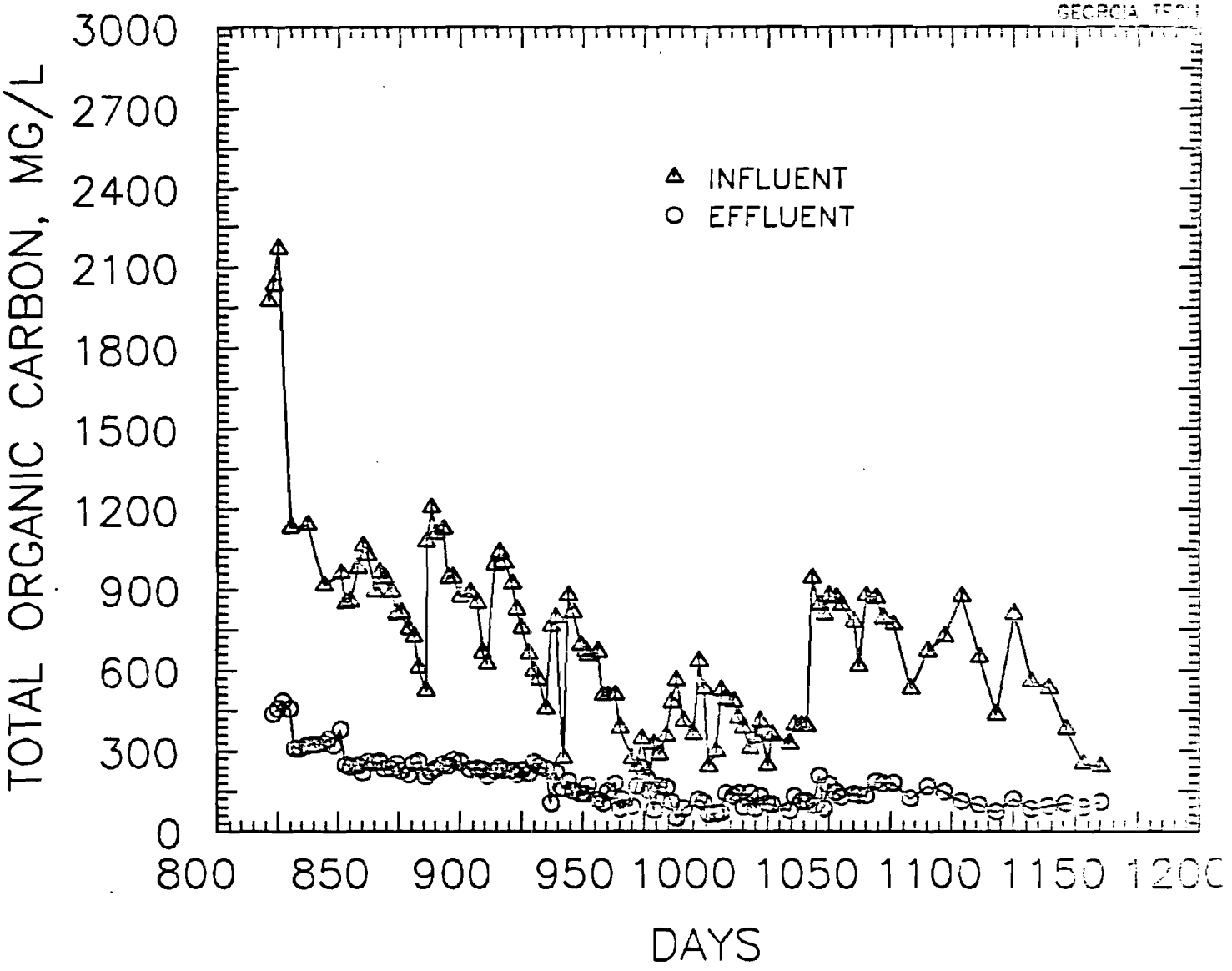
System 3, cycle Carbon Column Gas Composition

Figure 2



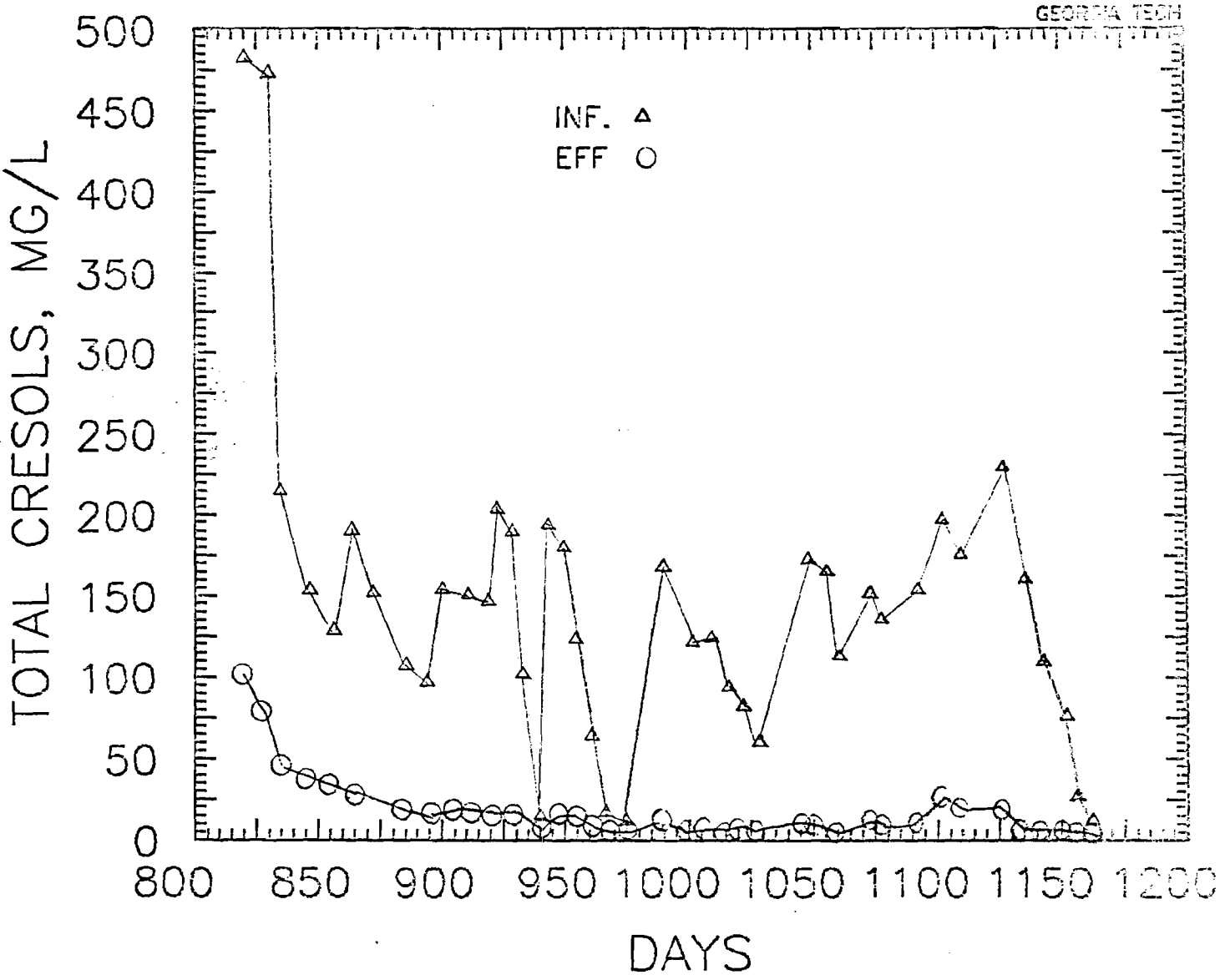
SYSTEM 3, PHENOL CONCENTRATION

Figure 3



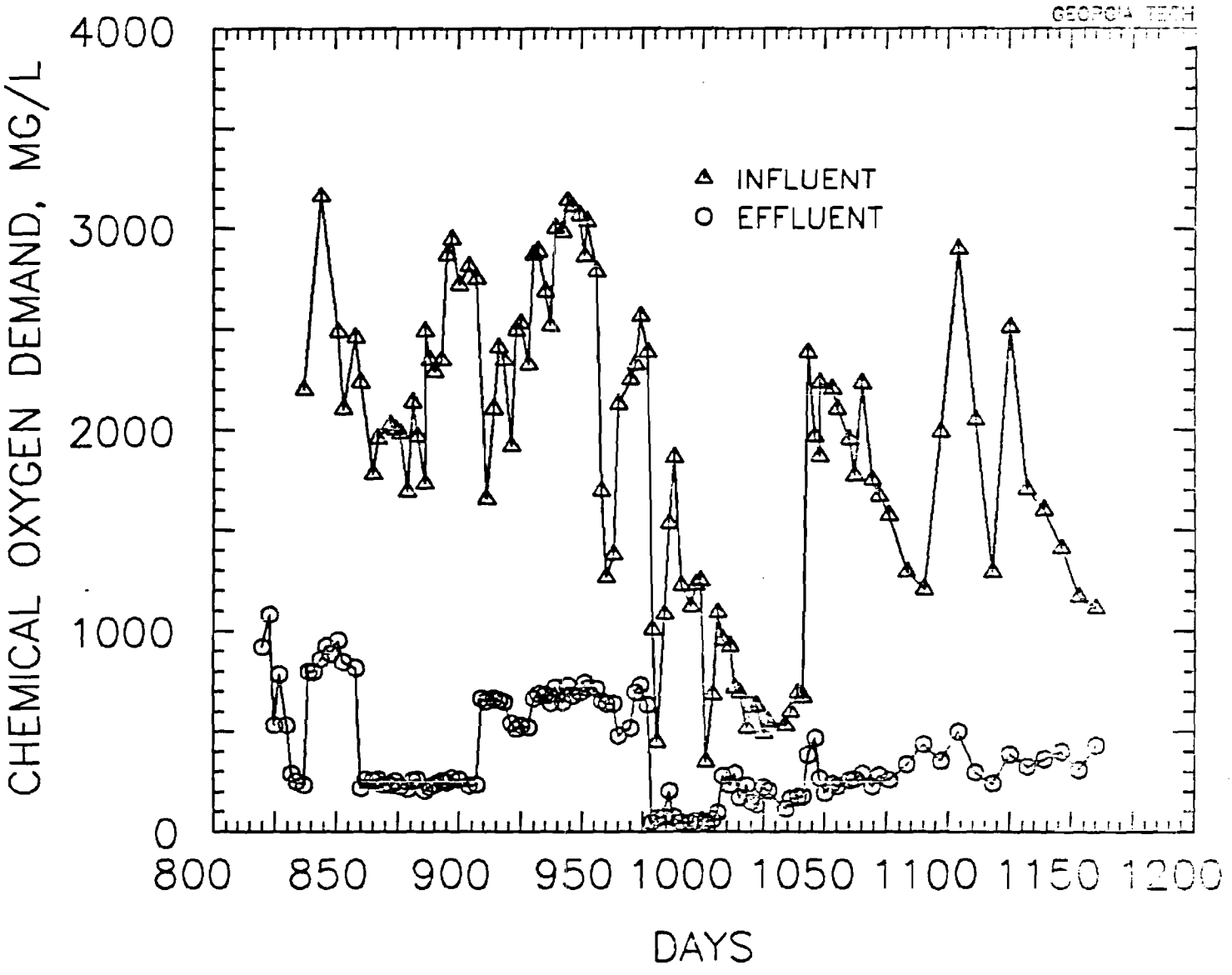
COLUMN 3A TOTAL ORGANIC CARBON

Figure 4



TOTAL CRESOLS OF COLUMN 3A

Figure 5



COLUMN 3A CHEMICAL OXYGEN DEMAND

Figure 6

B. Batch System

The 10 L completely mixed tank reactor has been maintained on a draw and fill basis, with granular activated carbon replacement, to serve as a source of seed for the serum bottle inhibition studies.

C. Serum Bottle Studies

Batch inhibition studies using serum bottles seeded from the 10 L batch reactor have been carried out on seven of the major constituents of coal gasification effluent used in this project. Of the compounds investigated to date and the concentration ranges used (Table 1) no major inhibition of the anaerobic process was observed. In some instances somewhat longer acclimation times were required before maximum gas production was obtained. However, this phenomena occurred both in the experimental as well as the control cultures indicating either a low level of organisms in the seed culture or a shock to the seed organism when the seed culture was transferred to the serum bottles.

TABLE 1

Compound	Concentration Added mg/L
phenol	150
o-cresol	150
m-cresol	150
p-cresol	150
hydantoin	250
5,5-dimethylhydantoin	400
5-ethyl-5-methylhydantoin	75

Gas production from serum bottles seeded from the 10 L batch reactor and spiked with only hydantoins indicated that the hydantoins were apparently being biologically degraded (Figure 7). However, the extremely long time (120 days) required to obtain maximum gas production indicated that a long acclimation period is apparently required in order for the microorganisms to adapt to the substrate.

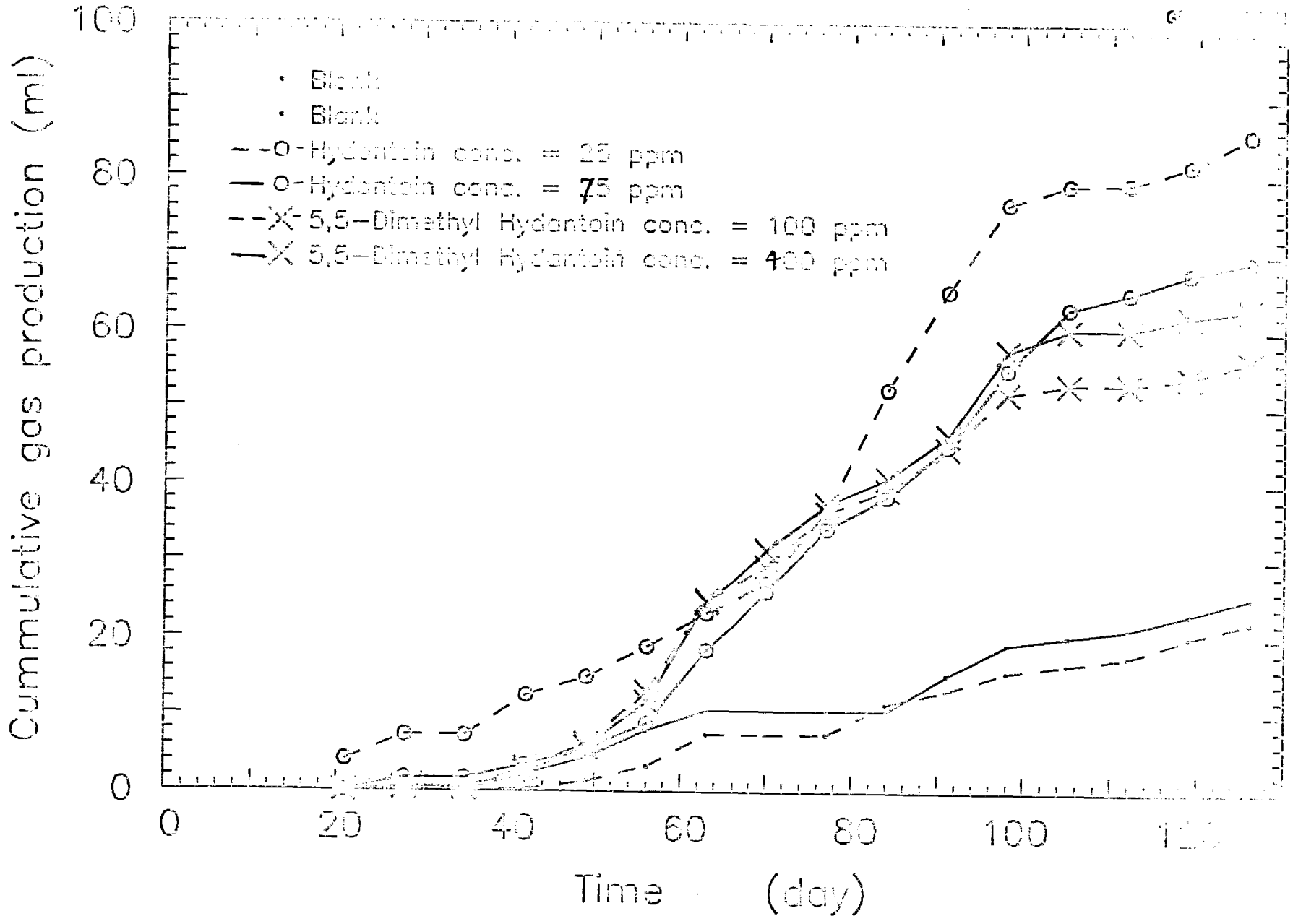


Figure 7 Cumulative Gas Production from Hydantoin Degradation

III. HYDANTOIN STUDIES

A. Adsorption

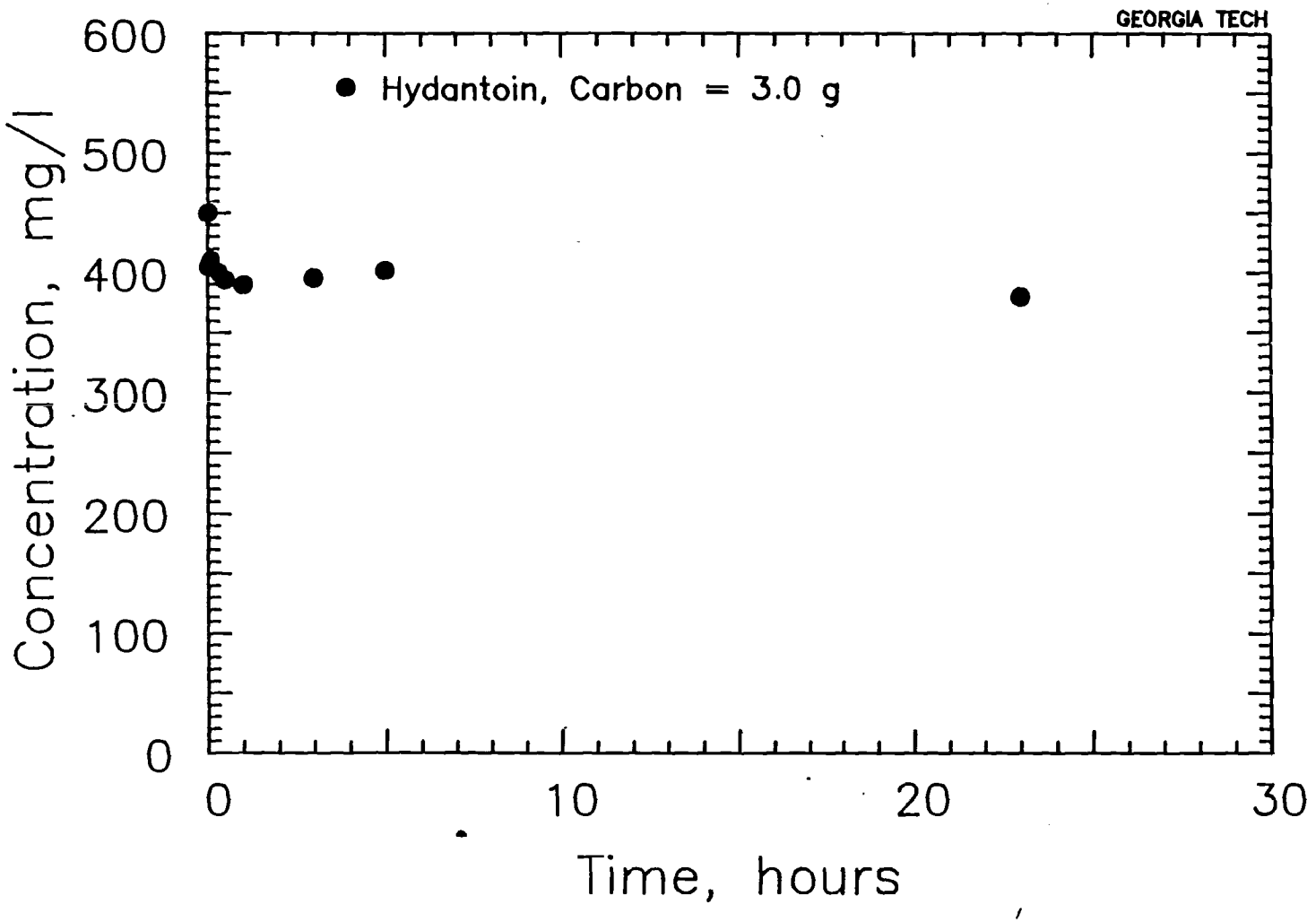
1. Single Solute Isotherms

Single solute kinetic and isotherm data were obtained for hydantoin, 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin. The kinetic data (Figures 8, 9 and 10) show that adsorption is relatively rapid. Equilibrium, with an initial concentration of 500 mg/L requires approximately two hours. The carbon capacity, at an initial concentration of 500 mg/L, ranges from 0.23 g/g for hydantoin up to 0.32 g/g for both 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin.

Single solute isotherms for the three compounds (Figures 11, 12 and 13) show a marked discontinuity as the size of the substituent groups on the parent compound increase.

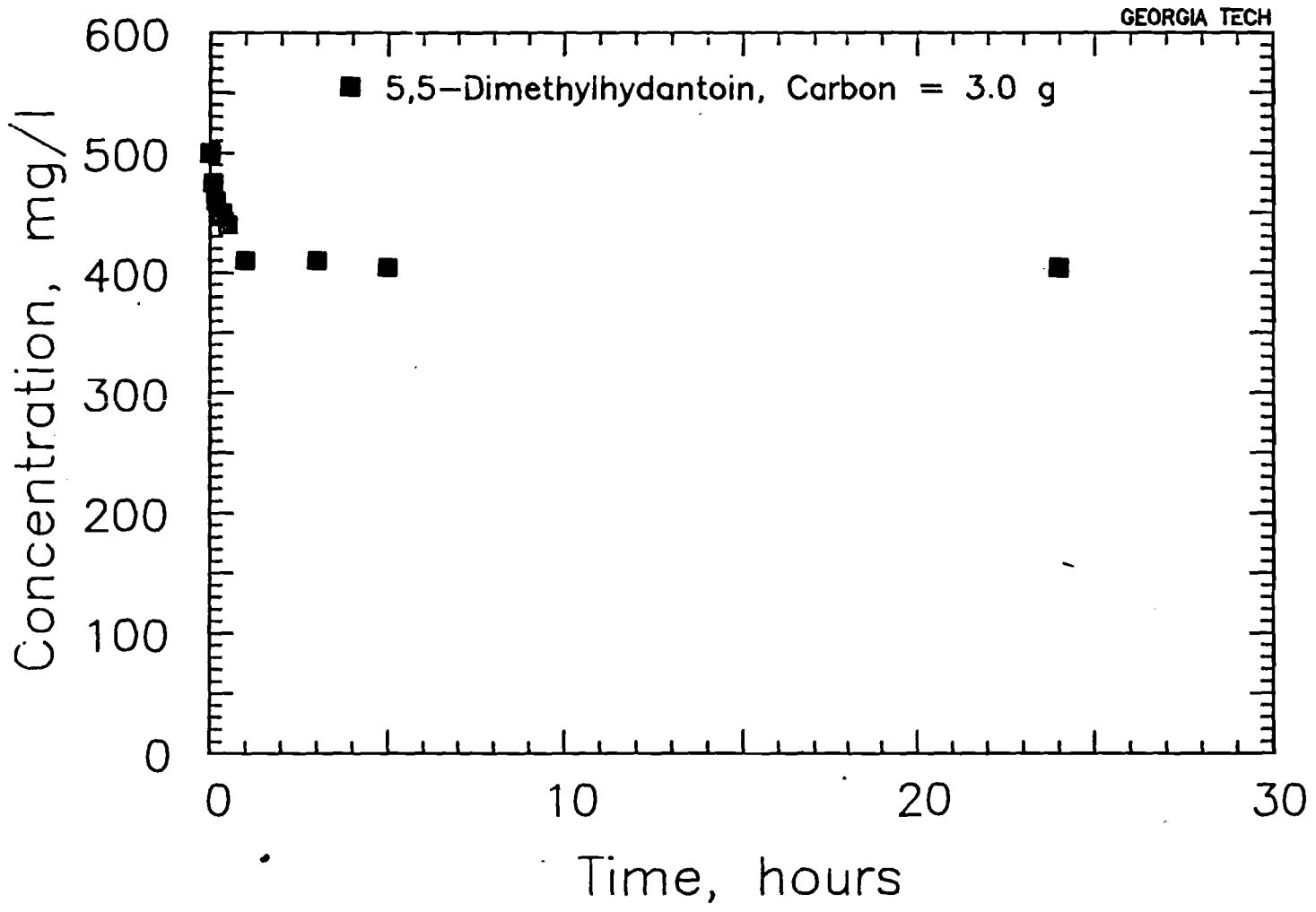
2. Column Studies

Column breakthrough studies were carried out using: a) the individual hydantoins, b) the three bisolute combinations, c) the one trisolute combination and d) pretreated coal gasification wastewater. As can be seen from Figures 14, 15 and 16 the single solute systems give the expected breakthrough. The breakthrough curve for the hydantoin - 5,5-dimethylhydantoin mixture (Figure 17) is very similar to the individual breakthrough curves for the two single solute systems indicating very little if any competition between these two compounds for adsorption sites on the granular activated carbon. However, the breakthrough curves for the remaining bisolute system (Figures 18 and 19),



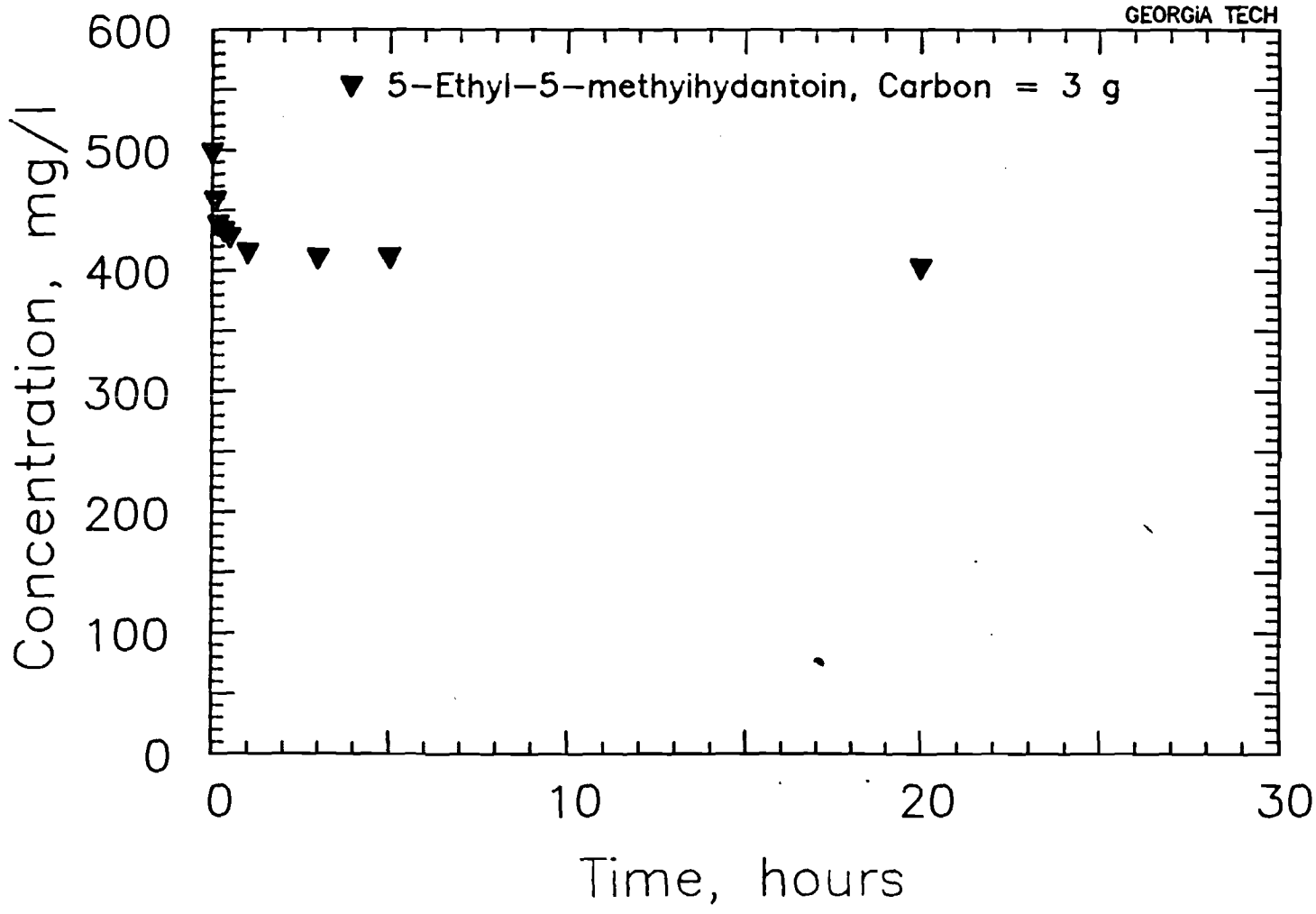
Batch Kinetic Curve for Hydantoin

Figure 8



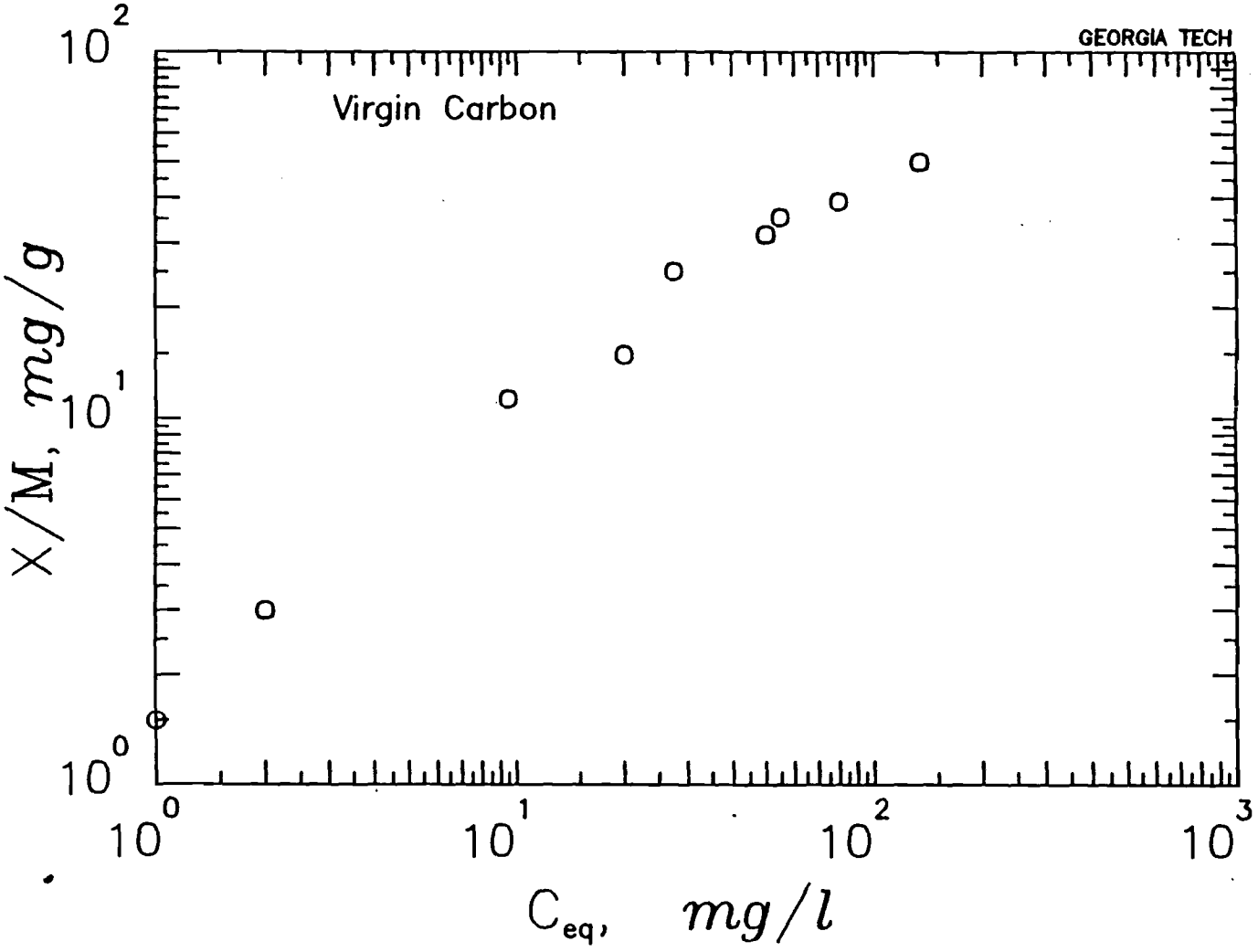
Batch Kinetic Curve for 5,5–Dimethylhydantoin

Figure 9



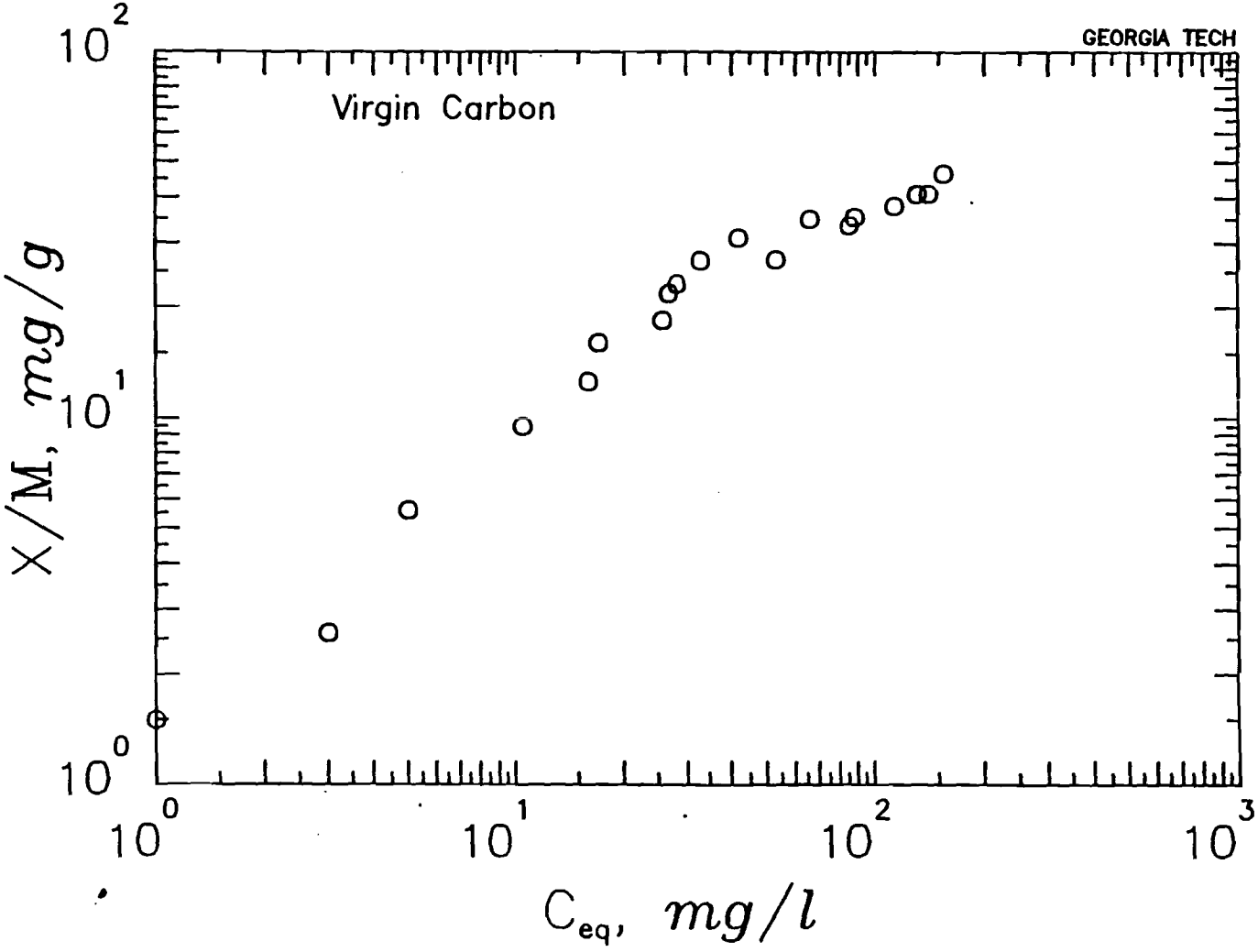
Batch Kinetic Curve for 5-Ethyl-5-methylhydantoin

Figure 10



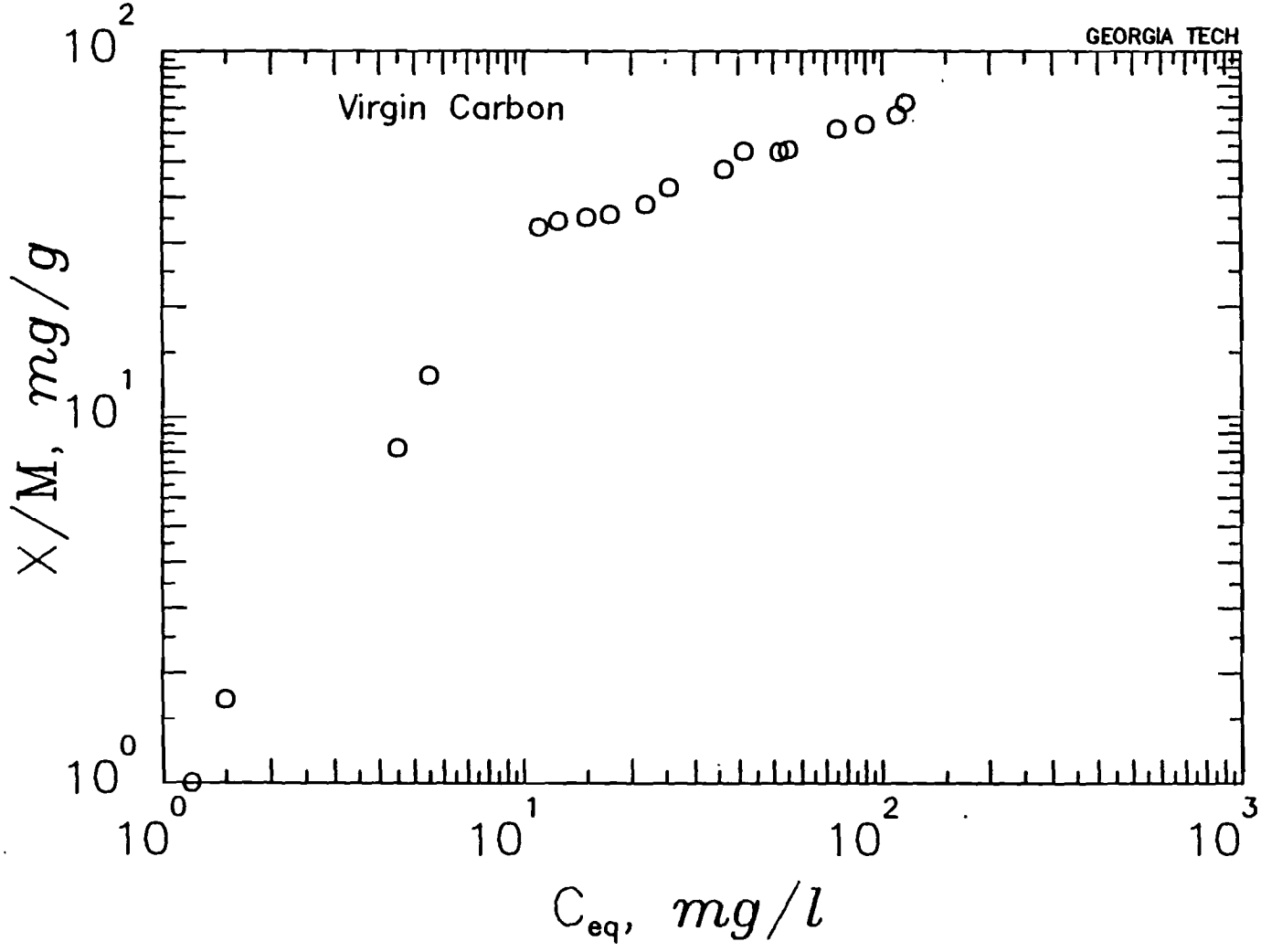
Adsorption Isotherm for Hydantoin

Figure 11



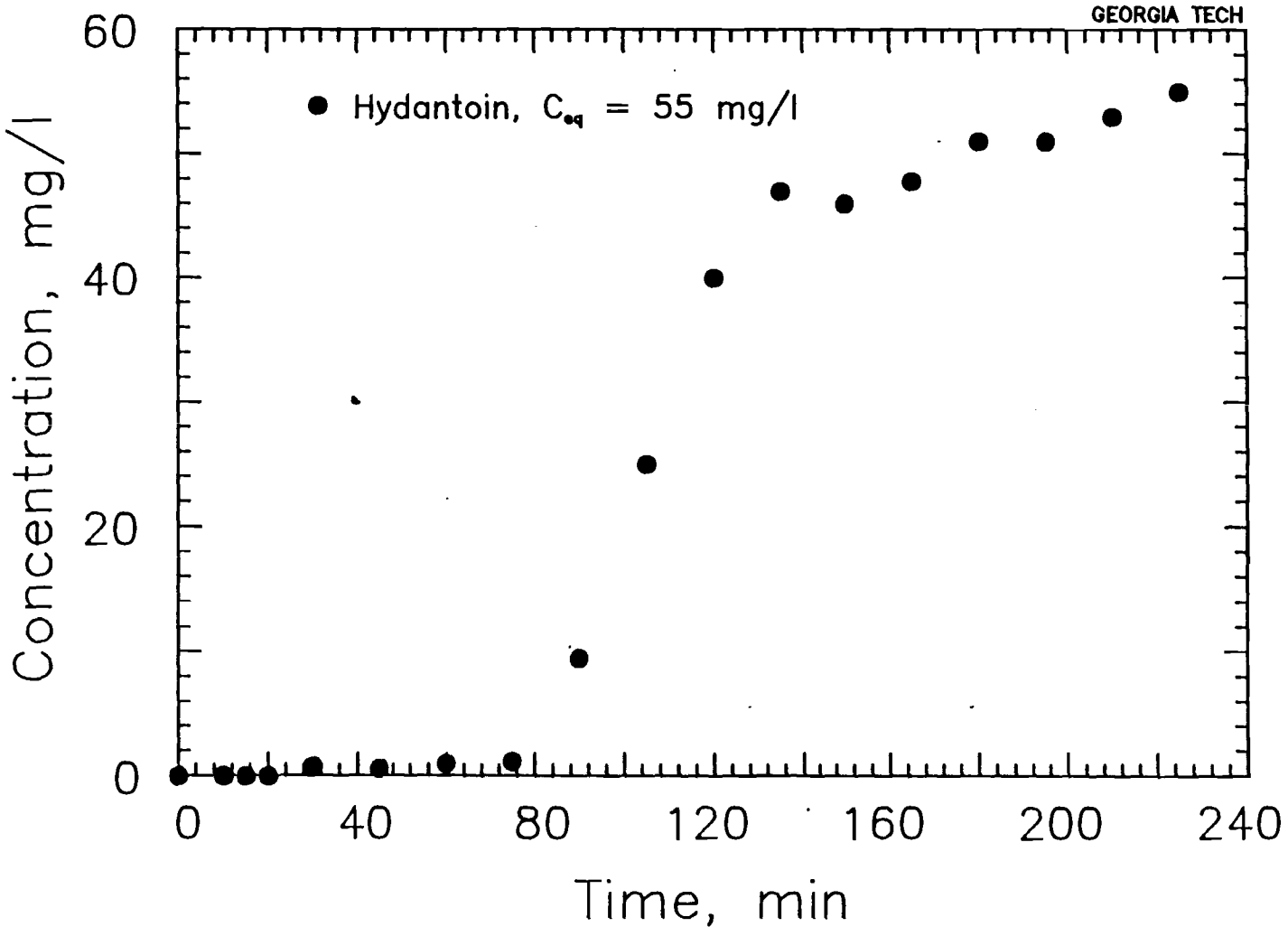
Adsorption Isotherm for 5,5 Dimethylhydantoin

Figure 12



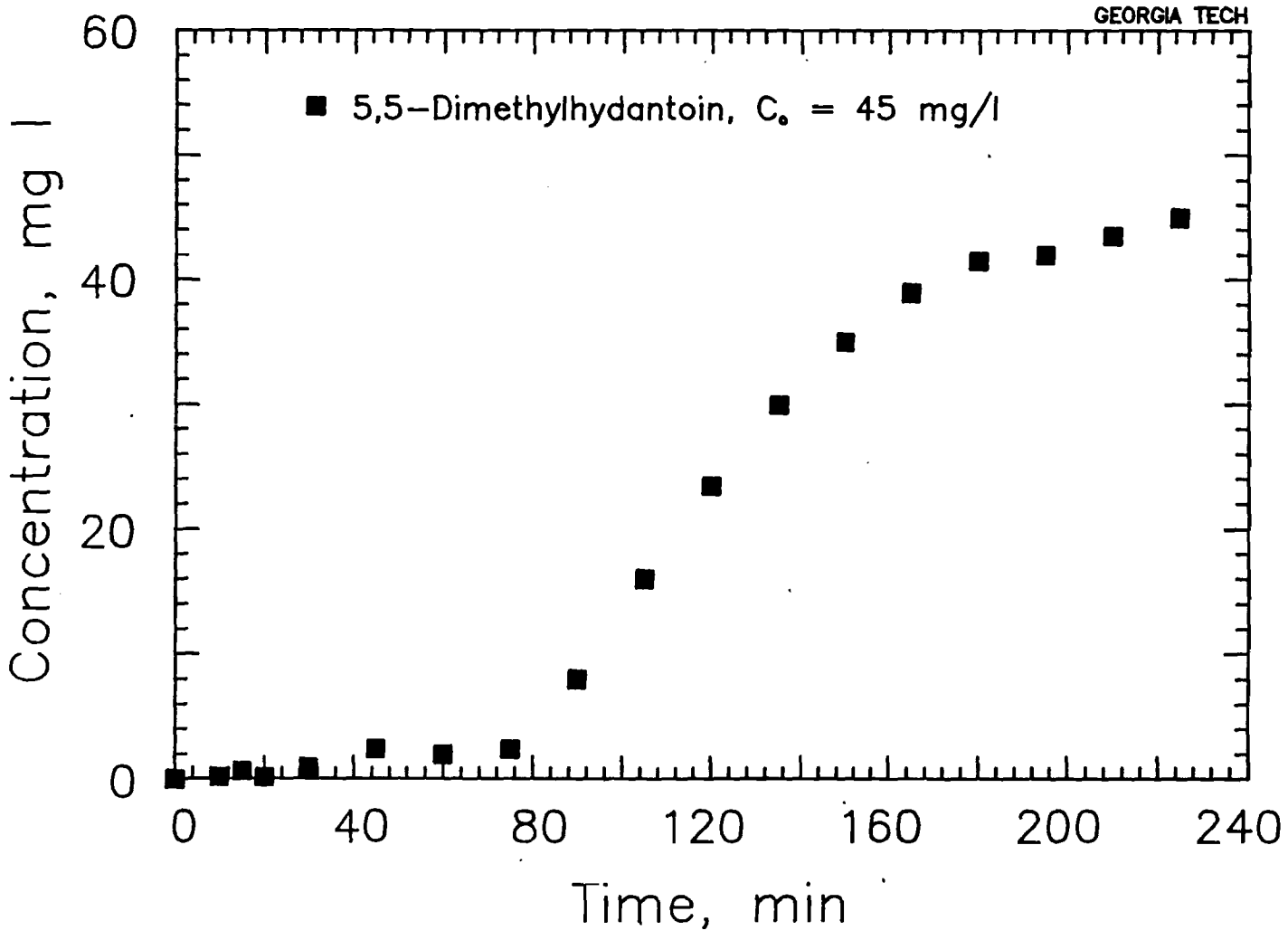
Adsorption isotherm for 5 Methyl 5 ethylhydantoin

Figure 13



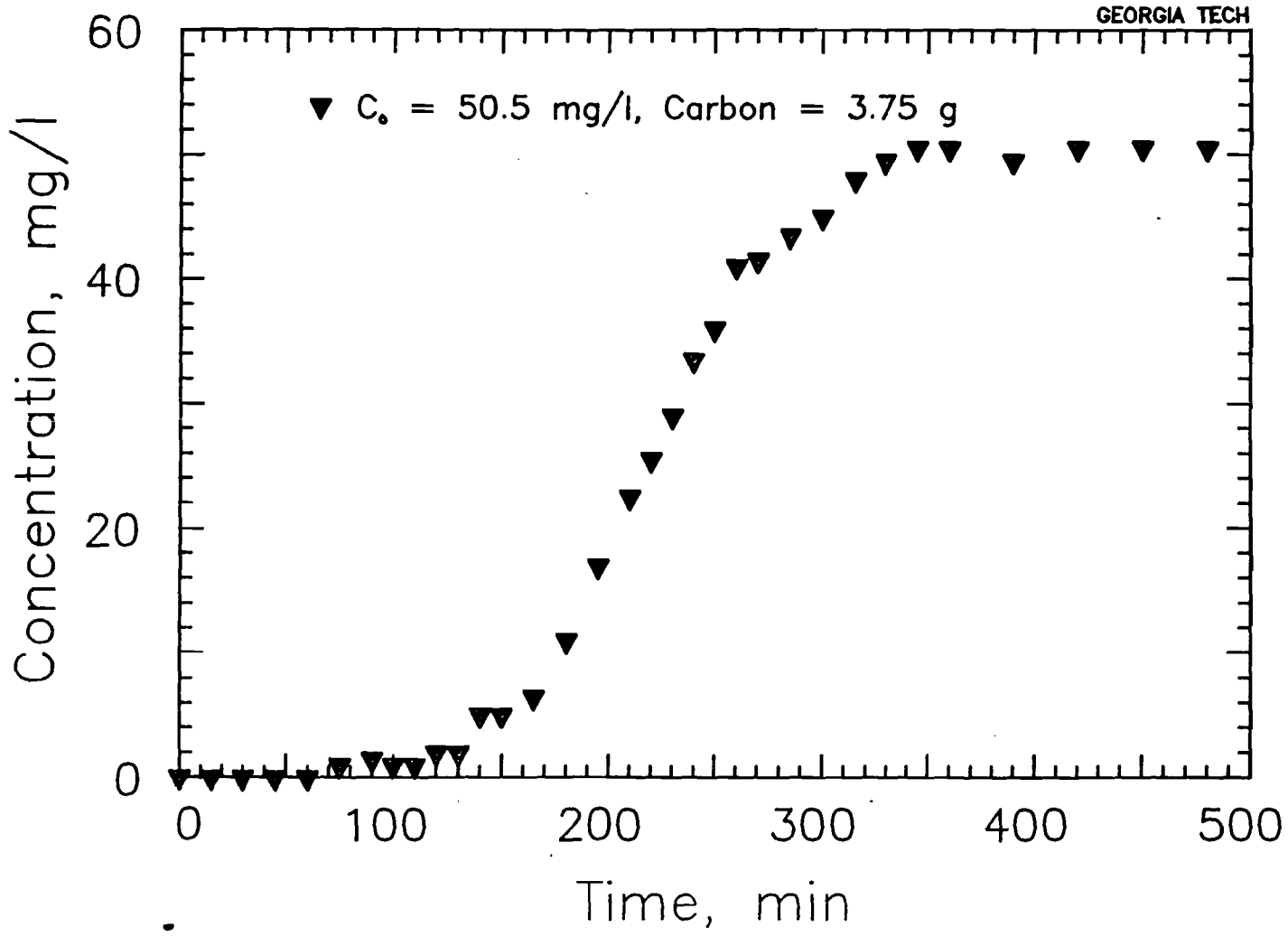
Breakthrough Curve for Hydantoin

Figure 14



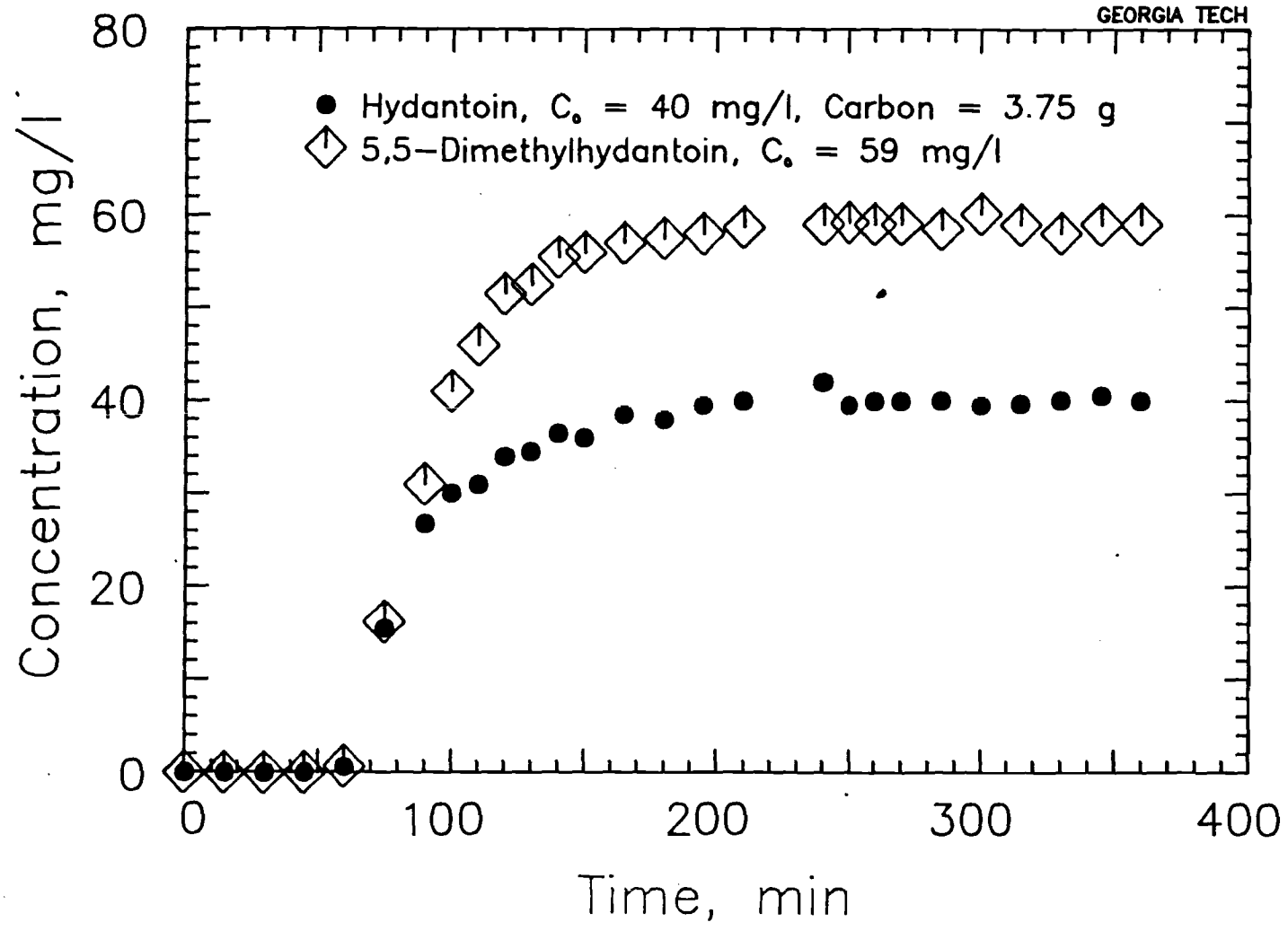
Breakthrough Curve for 5,5–Dimethylhydantoin

Figure 15



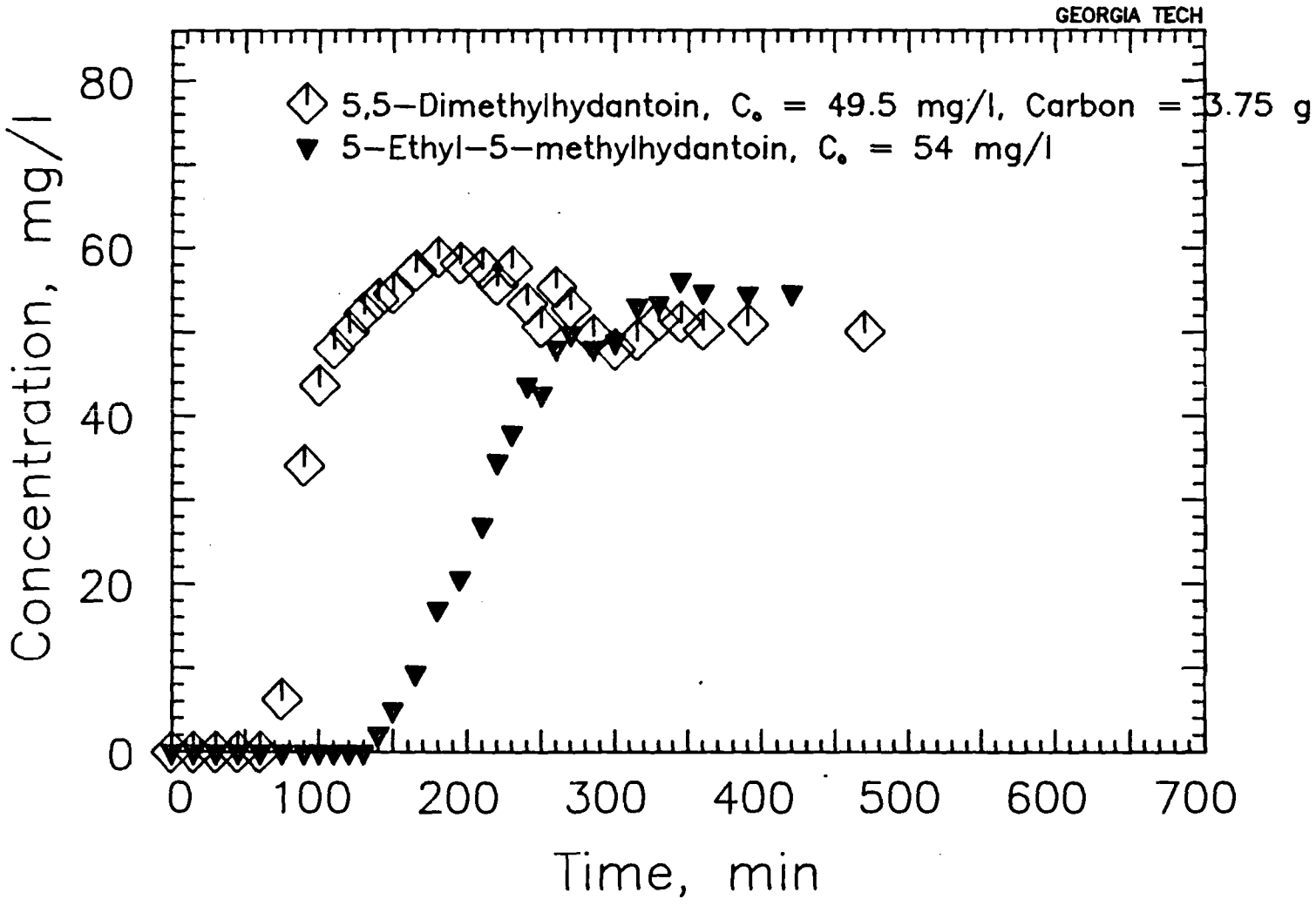
Breakthrough Curve for 5-Ethyl-5-methylhydantoin

Figure 16



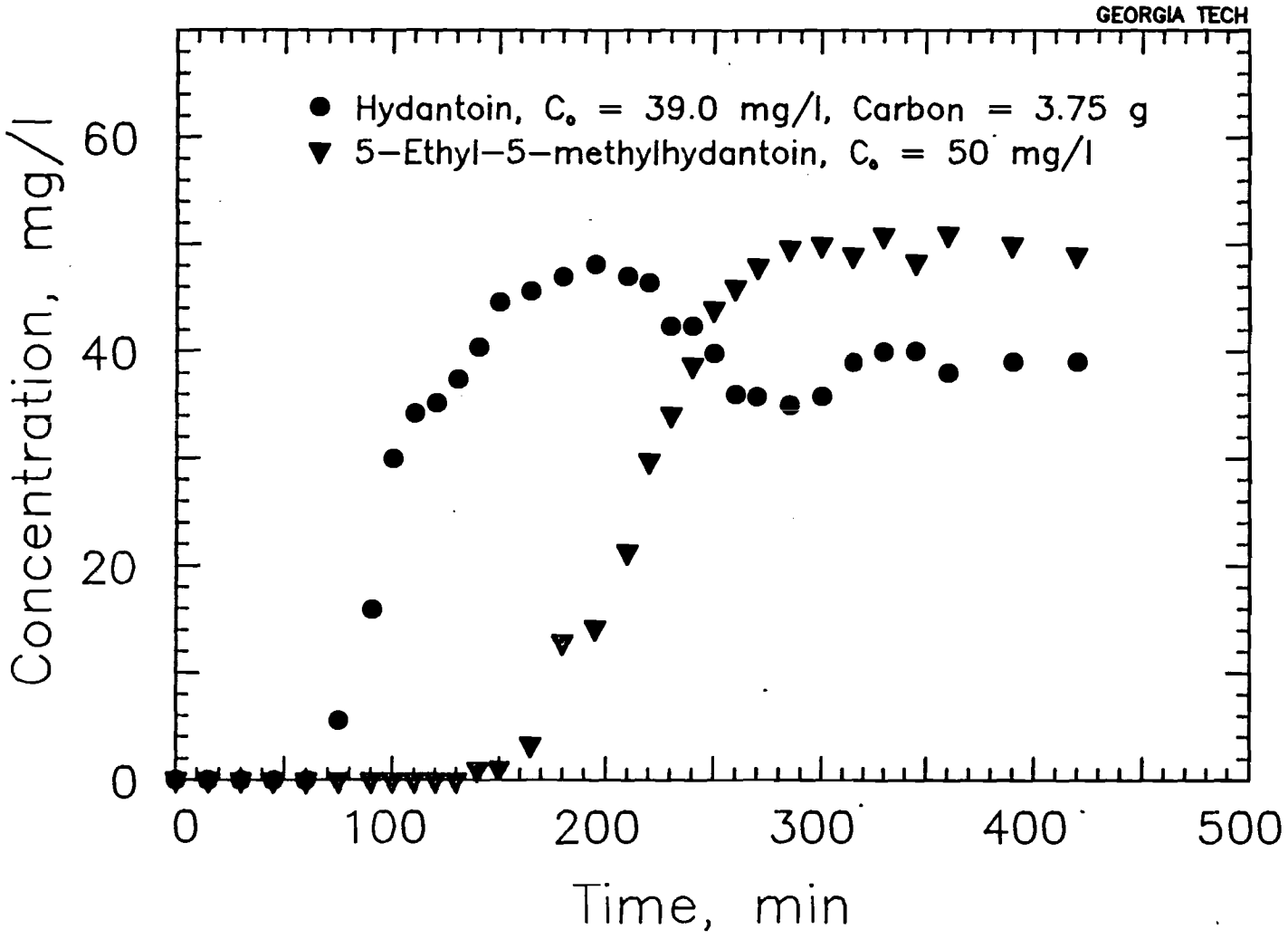
Bisolute Breakthrough Curve for Hydantoin
AND 5,5–Dimethylhydantoin

Figure 17



Bisolute Breakthrough Curve for 5,5–Dimethylhydantoin
AND 5–Ethyl–5–methylhydantoin

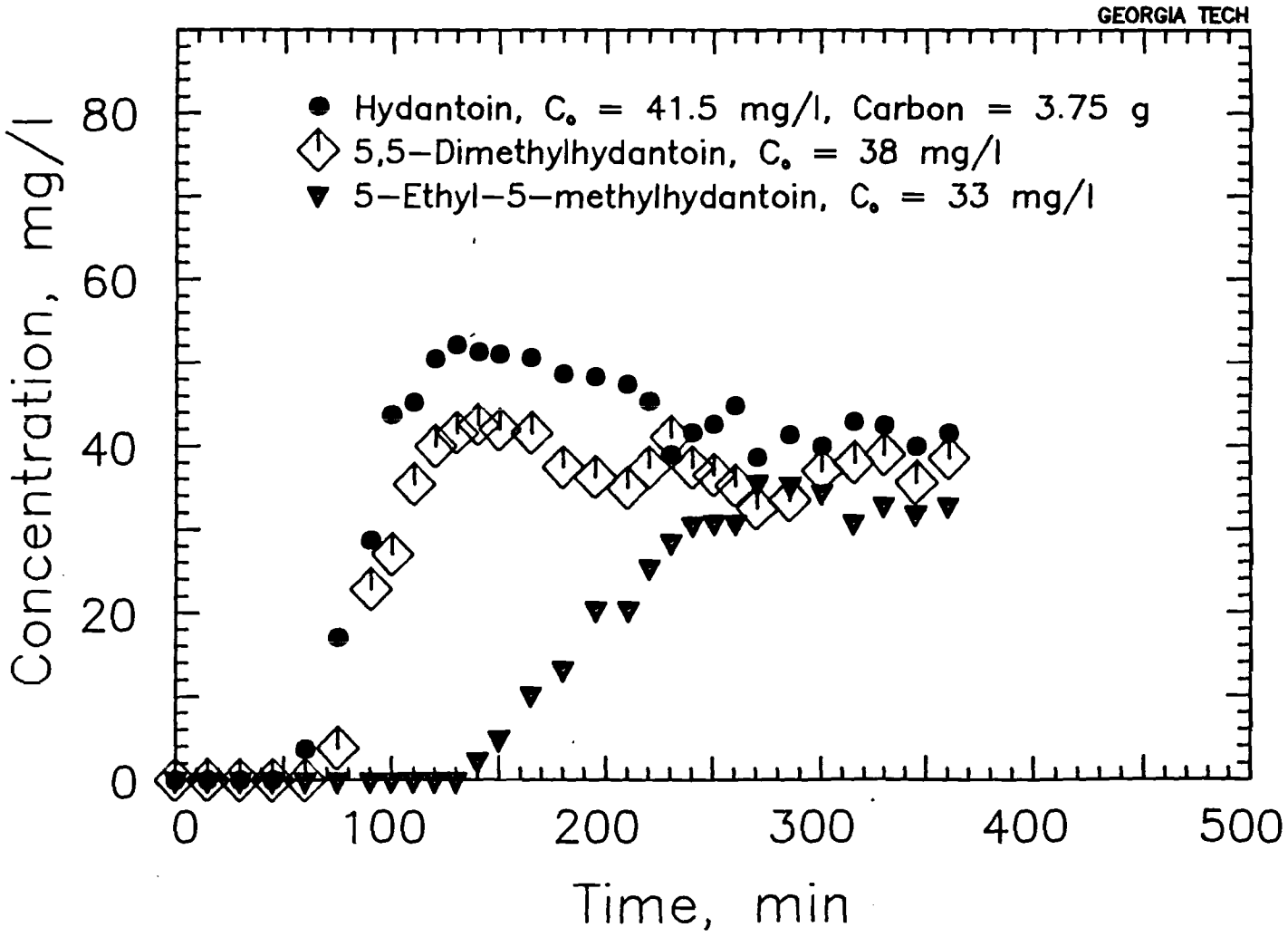
Figure 18



Bisolute Breakthrough Curve for Hydantoin
AND 5–Ethyl–5–methylhydantoin

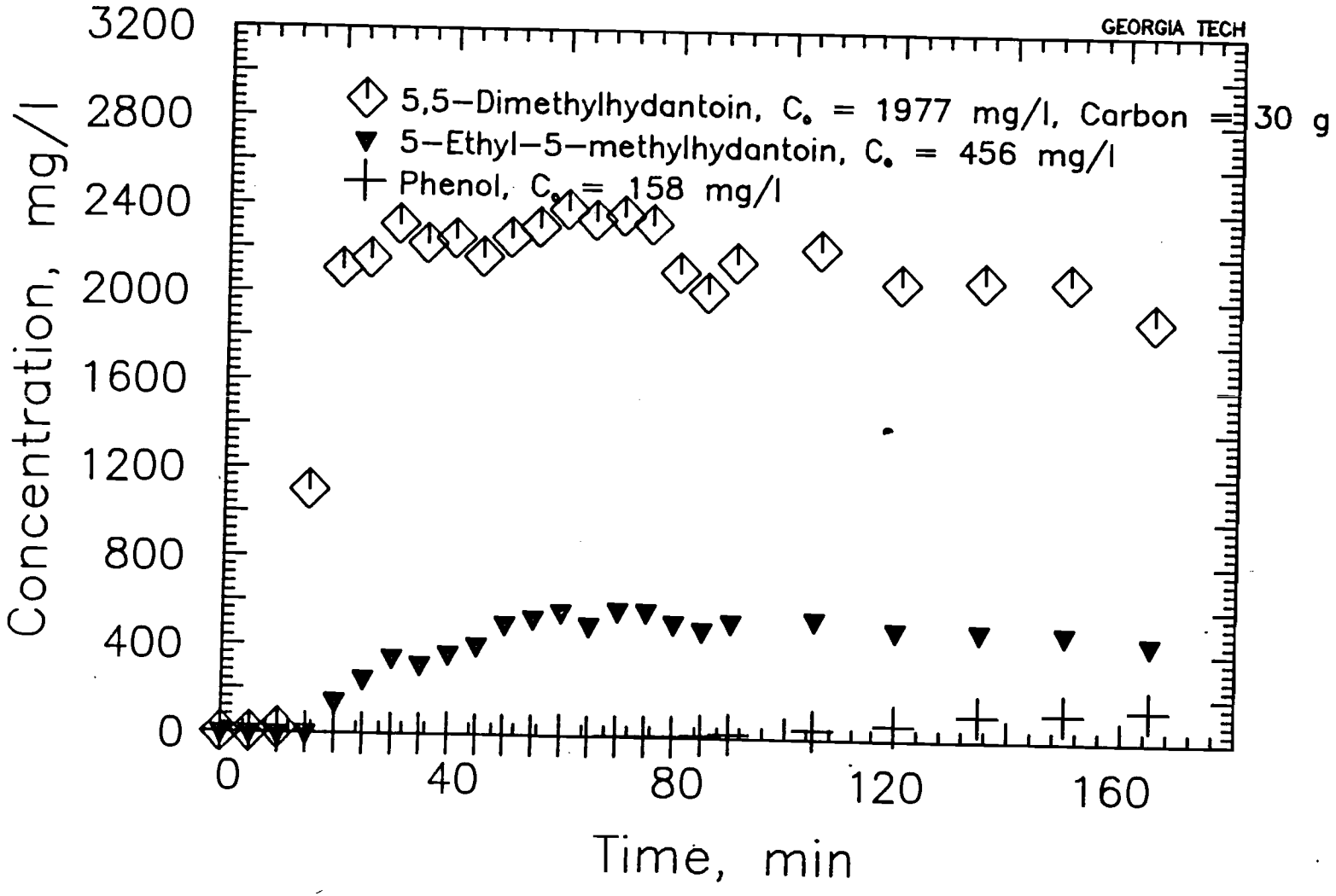
Figure 19

the trisolute system (Figure 20) and the pretreated wastewater (Figure 21) all show major competitive effects. In all of these systems the most weakly adsorbed compound is eventually displaced by more strongly adsorbed species when all the available adsorption sites have been occupied. This can be observed when the effluent concentration of the displaced compound is greater than its influent concentration. Therefore, removal or reduction in concentration of a specific compound will require careful monitoring of the system to assure that the carbon column is taken out of service and regenerated before the specific compound being removed is desorbed.



Trisolute Breakthrough Curve

Figure 20



Breakthrough Curve for Coal Gasification Wastewater

Figure 21

IV. FUTURE WORK

A. Serum Bottle Studies

Serum bottle inhibition studies will be continued with other specific compounds found in raw coal gasification effluents in order to ascertain if inhibition of the anaerobic process can be attributed to a particular compound or class of compounds.

B. Continuous Flow Studies

A granular activated carbon anaerobic filter, previously operated on dilute raw coal gasification effluents will continue to be operated utilizing pretreated wastewater as the feed. Adsorption and/or biodegradation of the hydantoins in this system will be studied.

C. Regeneration Studies

Adsorption-regeneration studies will be carried out using pretreated wastewater and selected solvents in order to determine the appropriate operational strategies for removing hydantoins from pretreated coal gasification effluent.

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This report summarizes the work performed during the period from January 1, 1985 through March 31, 1985 (Day 1187 to Day 1276) on the DOE research program on "Anaerobic Treatment of Gasifier Effluents - Inhibition and Fate of Hydantoin Studies" (Contract No. DE-AC18-81FC10297). The major efforts have been directed towards: 1) continuous flow anaerobic activated carbon filters for the treatment of solvent extracted-ammonia stripped gasifier effluent and 2) activated carbon adsorption followed by solvent regeneration for the treatment of solvent extracted-ammonia stripped gasifier effluent.

II. ANAEROBIC TREATMENT SYSTEMS

A. Inhibition Studies

Batch serum bottle inhibition studies have been completed for the major organic constituents found in raw gasifier effluents used in this study. The final three compounds investigated were the isomeric picolines (2-picoline, 3-picoline and 4-picoline). Gas production data from serum bottles innoculated with mixed liquor from an anaerobic batch reactor being fed diluted raw gasifier effluent and spiked with individual picolines showed that all three isomers caused severe inhibition of the anaerobic process.

Table 1 shows the concentrations of the picolines used in the mxitures when gas production was severly inhibited.

Table 1. Picoline Concentrations Causing Severe Inhibition

Compound	Concentration, mg/L
2-picoline	50
3-picoline	100
4-picoline	100

B. System III - Continuous Flow Studies

System III has continued to be operated in the continuous flow mode using pretreated wastewater at a feed flow rate of 2 mL/min since January 1, 1985.

The influent TOC concentration has been periodically increased in approximately 200 mg/L increments from 200 mg/L to 600 mg/L. This represents an increase from 14% wastewater to 41% wastewater. Effluent TOC concentrations have remained relatively constant during this period (Figure 1) giving TOC removals which have increased from approximately 50% to approximately 78%.

Hydantoin removal is also quite good with the system showing complete removal of 5-methyl-5-ethyl hydantoin and greater than 70% removal of 5,5-dimethylhydantoin. Almost complete color removal occurs and volatile acids in the effluent are extremely low, less than 50 mg/L total volatile acids.

However, gas production has been extremely low. The system has been checked for leaks and all which were found have been sealed.

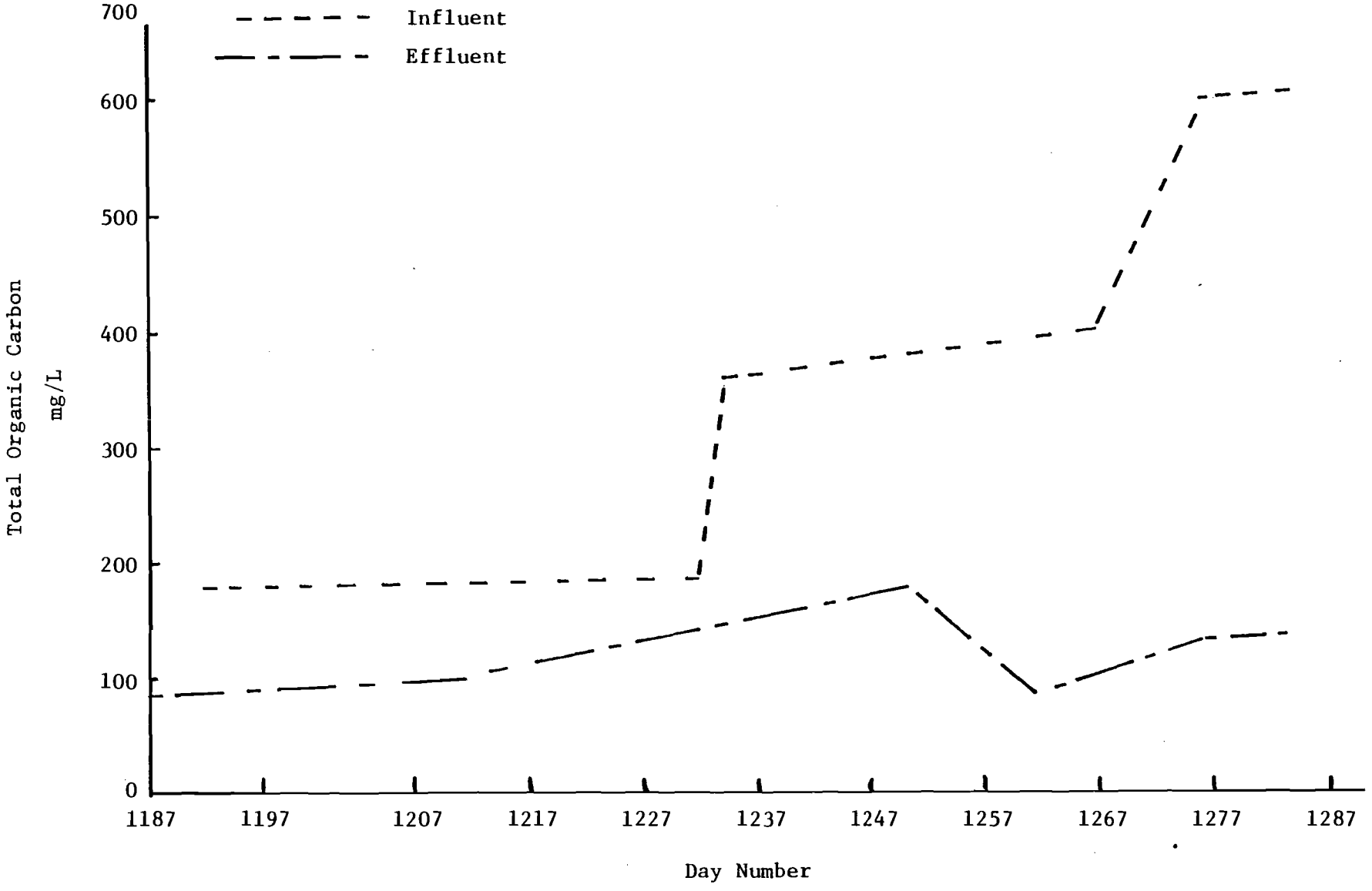

Figure 1. TOC Influent-Effluent, System 3

III. HYDANTOIN STUDIES

Continuous flow adsorption-solvent regeneration has been carried out using full strength pretreated gasifier effluent as the adsorbate and 0.1 M NaOH as the regenerant.

Both TC and hydantoin analyses were performed on the column effluent samples. Although the data for breakthrough and completion of regeneration were essentially identical (Figures 2,3,4 and 5) the results of an attempted carbon balance were in error. More TC was extracted from the exhausted column than was adsorbed during the exhaustion phase. This result is believed to be due to the fact that the regenerant (0.1 M NaOH) adsorbed atmospheric CO_2 during the regeneration cycle and gave erroneously high TC values.

All future adsorption-regeneration cycles with aqueous solvents will be monitored for TOC and/or hydantoins.

Regenerated activated carbon showed a marked loss in adsorption capacity (Figure 2). Approximately 30% of the carbon capacity was lost in the first regeneration cycle. This indicates that the solvent used (in this case 0.1 M NaOH) was incapable of displacing all of the adsorbed organic species from the carbon surface. Extrapolated over several adsorption-regeneration cycles this would eventually lead to total loss of the carbon's adsorption capacity. This would then necessitate either complete replacment of the carbon or using some other means of regeneration. This, if the capacity loss per cycle was very small, might be acceptable. However, a 30% adsorbtive capacity loss per cycle is not acceptable. Therefore, it can be concluded that 0.1 M NaOH is not an appropriate or acceptable regenerant for this system.

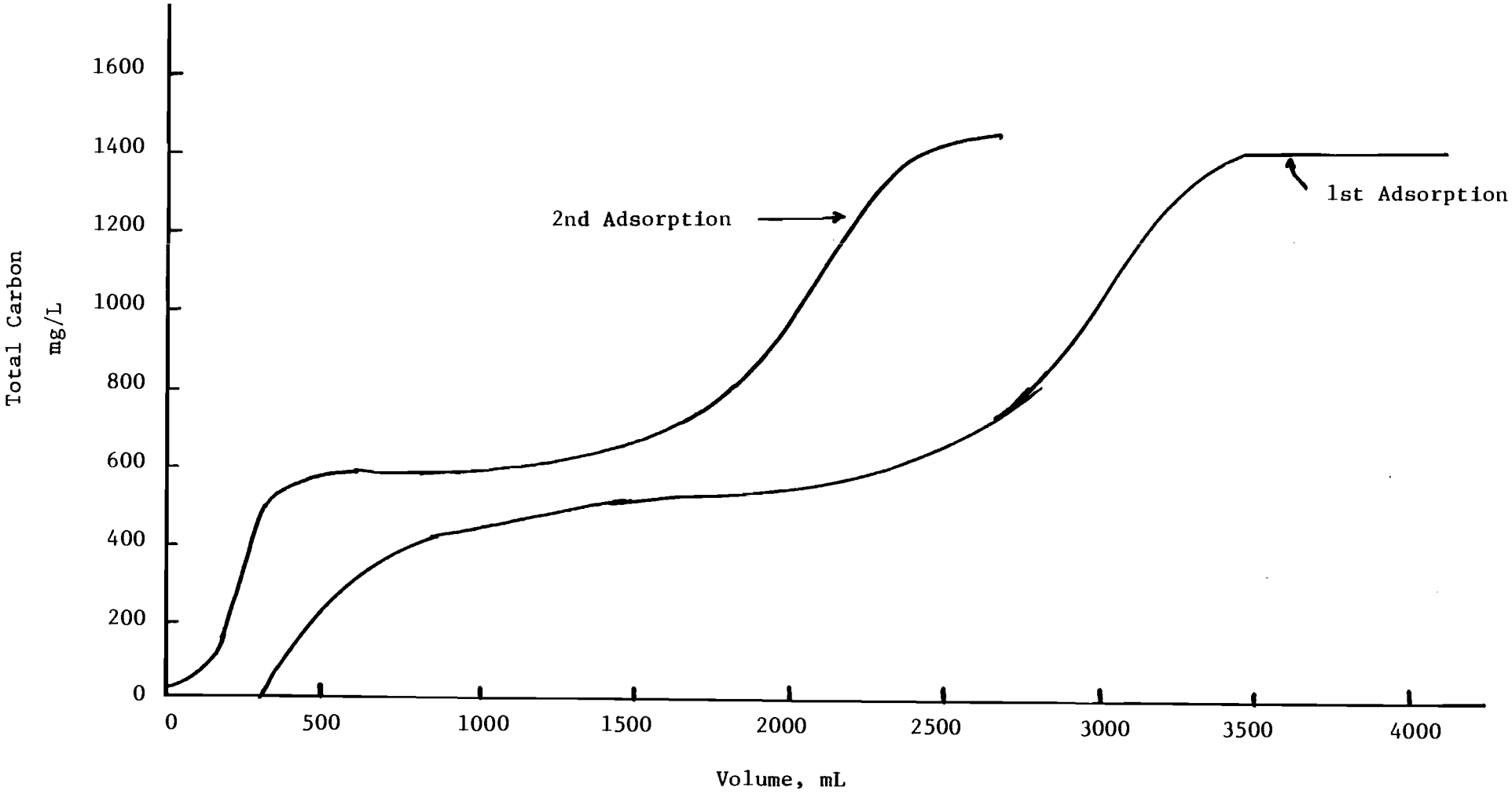

Figure 2. Carbon Adsorption Breakthrough Curve

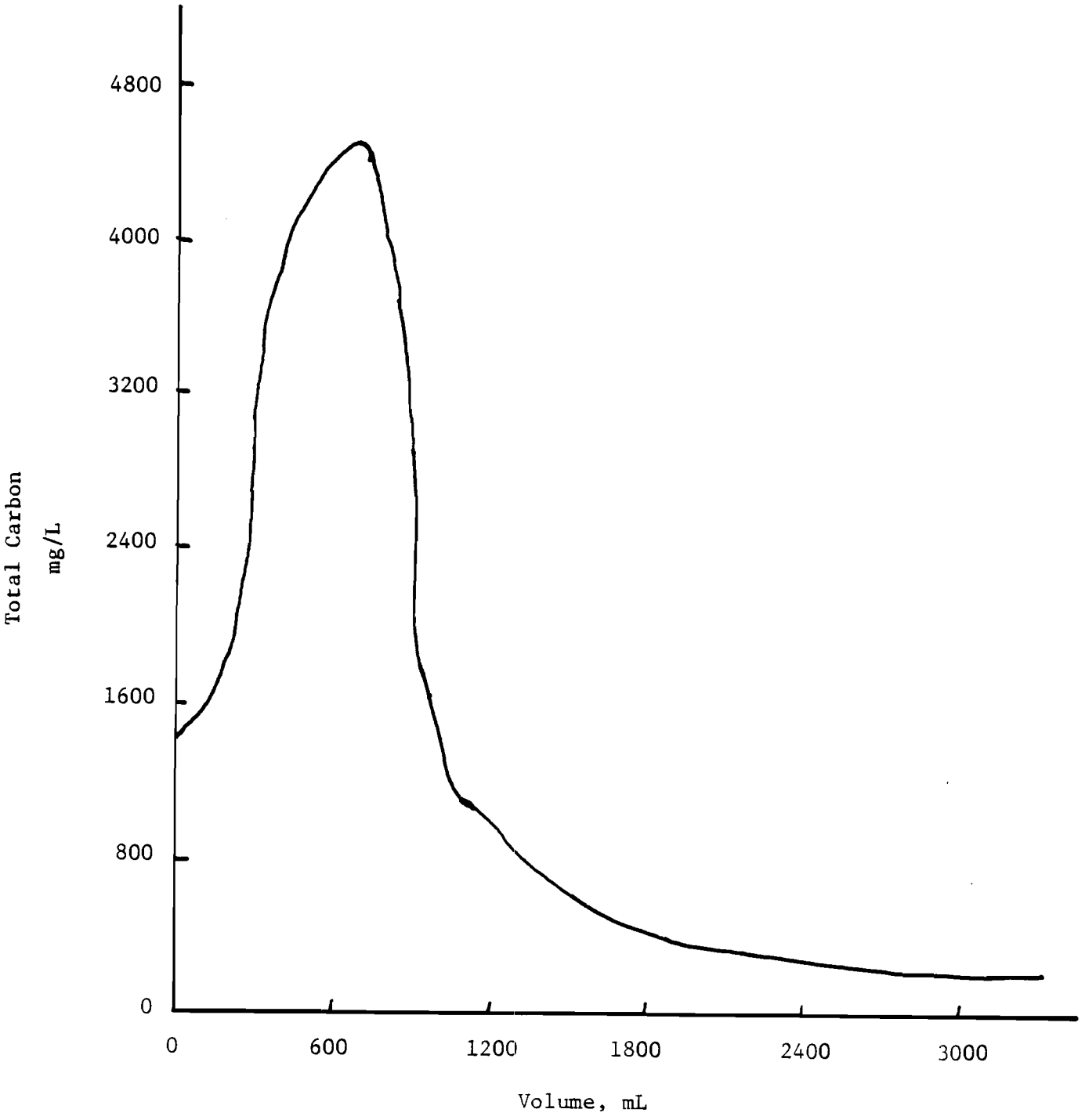

Figure 3. Regeneration with 0.1 M NaOH

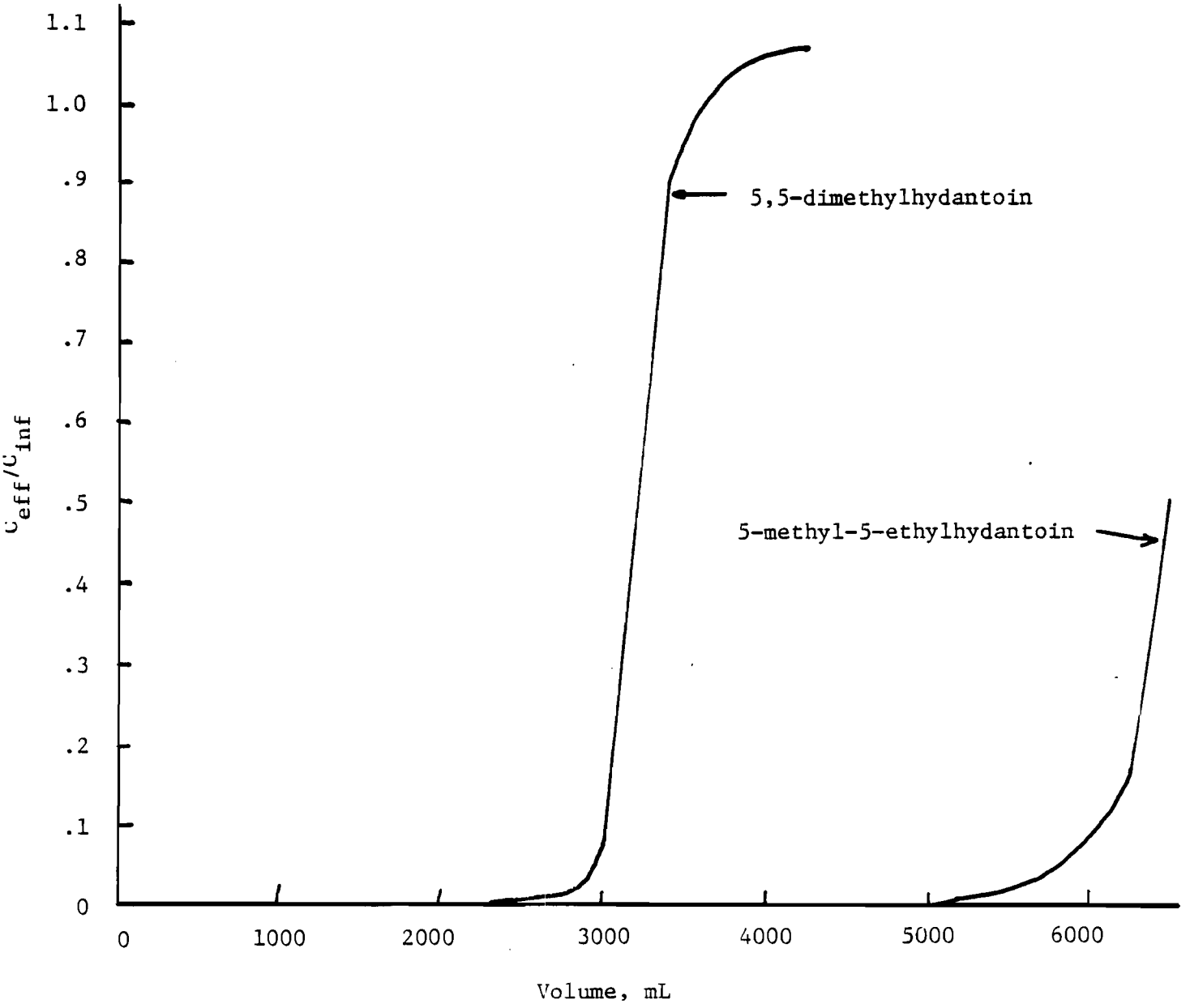

Figure 4. Hydantoin Breakthrough Curve, 1st Adsorption

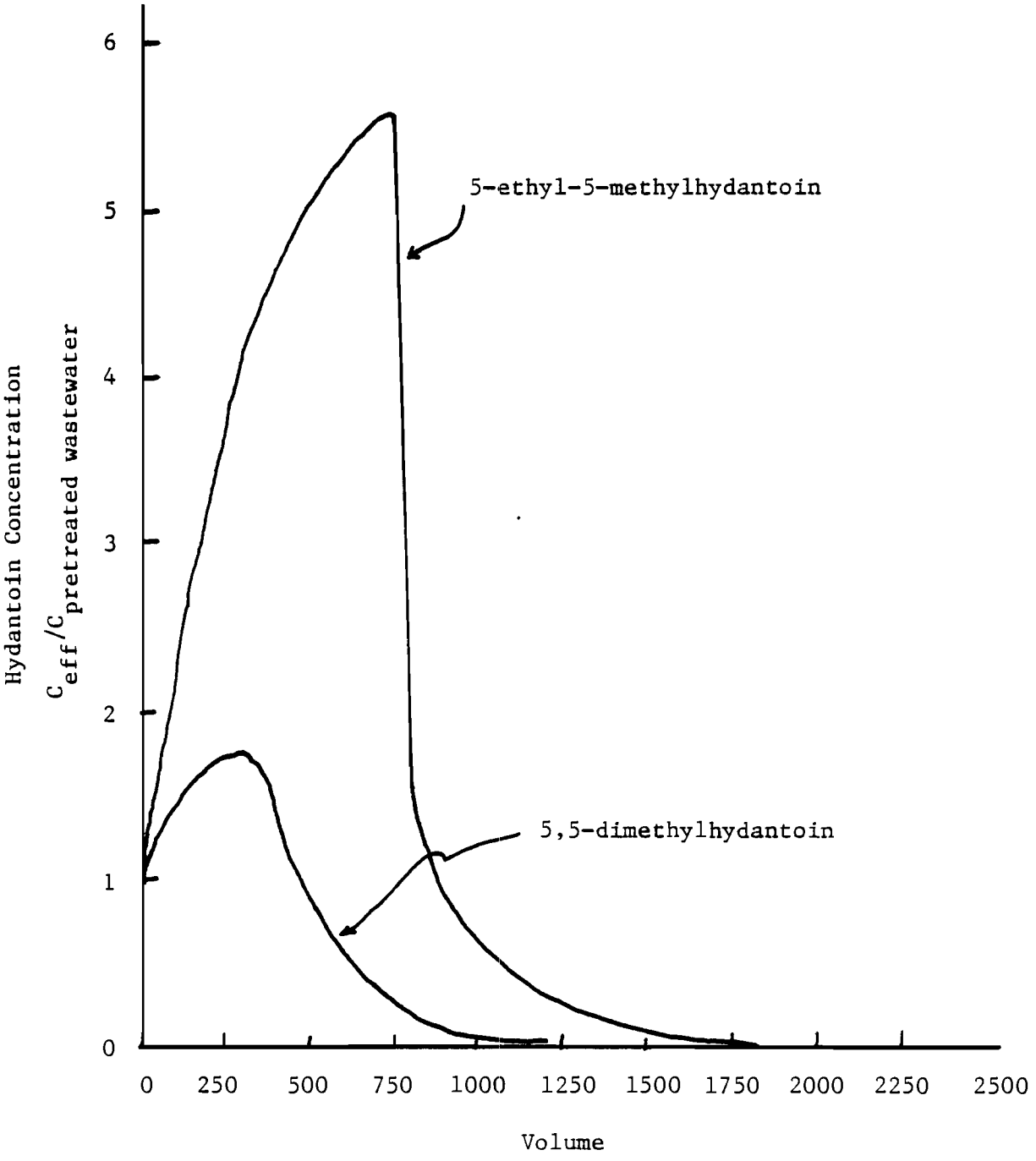

Figure 5. Regeneration with 0.1 M NaOH

IV. FUTURE WORK

A. Continuous Flow Study

Influent concentrations of pretreated wastewater will continue to be periodically increased until the system is receiving full strength wastewater. Effluent TOC, COD, VA, and hydantoins will be monitored to evaluate the performance of the reactor.

A different gas collection system is under construction and will be installed as soon as it is available.

If no gas is produced, but effluent TOC and other values remain relatively constant, an attempt will be made to seed the reactor with a different source of anaerobic microorganisms.

B. Adsorption-Regeneration Studies

Adsorption-regeneration cycles will be carried out using fresh carbon and other solvents in order to determine if an appropriate solvent can be found which will regenerate either the total adsorption capacity of the carbon or will minimize the adsorption capacity loss to an acceptable level.

IMPLEMENTATION PLAN

for

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

by

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August 1981

DOE Contract No. DE-AC18-81FC10297

I. RATIONALE

A. Problem Description

Current and projected wastewater treatment systems for coal gasification wastewater usually incorporate the use of aerobic biological wastewater treatment processes. Aerobic biological processes have several undesirable features when used to treat coal gasification wastewaters. These include:

i. the processes are energy intensive;

ii. the processes exhibit instabilities induced by concentration and and composition variations in the wastewater;

iii. the processes frequently show inhibition due to various constituents (e.g., ammonia, thiocyanate, phenol) in the waste stream; and,

iv. many constituents found in coal gasification wastewaters show little or no removal by aerobic treatment processes.

II. PROPOSED RESEARCH

The proposed research will evaluate the biological treatability of coal gasification wastewaters utilizing two upflow anaerobic filters operated in series followed by aerobic nitrification as principal process elements. The two-stage anaerobic filter system will consist of an initial roughing filter packed with Raschig Rings followed by a column packed with granular activated carbon and provided with recirculation capabilities to allow for expansion and/or fluidization of the carbon bed. The project will investigate maximum wastewater loadings obtainable with both raw and pretreated coal gasification wastewaters and the effect of recirculation rate on system performance.

Because of the high ammonia nitrogen content of the wastewater, its removal will be addressed using both biological and physical treatment techniques. The biological nitrogen removal system will include at least nitrification and

possibly denitrification. This system will be coupled with other complementary physical treatment processes i.e., pretreatment by gas stripping and solvent extraction.

To accommodate the objectives of the proposed research, it will be divided into four phases.

Phase I: Characterization of Gasifier Wastewater; Analytical Procedures

Wastewater obtained from the Grand Forks Energy Technology Center in Grand Forks, North Dakota will be comprehensively characterized in order to obtain data necessary for monitoring the overall efficiency of each projected treatment process as well as determine the ensuing removal of specific wastewater constituents.

Procedures for analysis of the wastewater influents and effluents will be subdivided into the following catagories:

i. gross parameters;

ii. specific inorganic species; and,

iii. specific organic species.

Parameters to be determined in each catagory, their significance, methods of analysis, and quality assurance/quality control techniques will include the following:

a. Gross Parameters

Total alkalinity, five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC), total dissolved solids (TDS), conductivity, oxidation-reduction potential (ORP) and pH will be determined using procedures found in Standard Methods for the Examination of Water and Wastewater, 15th Edition. These analyses will be used to determine any precautions or wastewater adjustments necessary prior to use of the wastewater as a substrate for biological treatment. They will also assist in determining pretreatment requirement and in evaluating the general performance of the pretreatment as well as the overall treatment processes.

b. Specific Inorganic Analysis

Inorganic species to be determined include CN^-, SCN^-, S^{-2}, NH_3, PO_4^{-3}, NO_2^-, NO_3^- and constituent metal ions. Results from these analyses will be used to determine any necessary nutrient supplements which need to be added, to ascertain possible inhibitory effects, and to evaluate the effectiveness of the pretreatment processes and the efficiency of both the anaerobic and the nitrogen conversion/removal systems.

Initially, the inorganic anions and ammonia will be determined by use of Standard Methods procedures, while the metals will be determined by atomic absorption spectrophotometric techniques. After the initial analyses are completed, some effort will be devoted to developing ion chromatographic techniques for the anion analyses in order to decrease the level of effort necessary to provide routine anion monitoring.

c. Specific Organic Analysis

The initial analysis of the wastewater for organic compounds will include those compounds on the EPA Priority Pollutant List together with other compounds which have previously been found in coal gasification wastewaters. Special emphasis will be placed on determining the presence of phenols, cresols, xylenols, polynuclear aromatic hydrocarbons, biphenyls, aromatic amines and polycyclic hydroxycompounds. Data from the initial wastewater characterization will be used to select specific compounds to monitor across both the pretreatment and overall biological treatment processes.

Current state-of-the-art methodology utilizing purge and trap, solvent extraction (both liquid-liquid and vaper phase techniques), along with size exclusion chromatography will be utilized for initial sample clean-up and separation prior to specific analysis. Liquid chromatography, gas chromatography and gas chromatography/mass spectrometry techniques will be used to identify compounds.

d. Quality Assurance/Quality Control

All analyses will be subjected to a rigorous quality assurance/quality control (QA/QC) procedure which will include method validation, analysis of duplicate samples, analysis of known samples, analysis of samples spiked with known compounds and surrogates, and other accepted procedures for assuring the receipt of reliable analytical data.

Phase II: Pretreatment of Gasifier Wastewater

Phase II will examine the effects of physical-chemical pretreatment of the raw coal gasification wastewater prior to anaerobic biological treatment. Pretreatment efforts will be directed toward two physical-chemical processes with an evaluation of the efficiency and appropriate sequence for the two pretreatment processes. This pretreatment will include air stripping for NH_3 removal and solvent extraction for reduction of the quantity of insoluble and/or toxic/inhibitory organic compounds prior to anaerobic biological treatment.

a. Air Stripping

Ammonia in high concentrations can be either inhibitory or toxic to biological treatment systems. Therefore, pretreatment of the raw wastewater to reduce the concentration of ammonia will be investigated. This effort will consist of determining the effect of pH adjustment on removal of NH_3 to prevent possible NH_3 inhibition or toxicity in the anaerobic biological treatment systems. At the same time TOC removal will be monitored to asses the possible removal of volatile organic compounds in the gas stripping process. If the TOC removals are sufficiently large, steps will be taken to identify the type and quantities of specific organic compounds removed in this pretreatment step.

b. Solvent Extraction

Solvent extraction will be utilized to: a) remove the water insoluble organic fraction from the waste stream which could interfer with the anaerobic biological

treatment process; and, b) to reduce the concentration of soluble organic and inorganic species which may be inhibitory or toxic to the anaerobic biological system.

Solvent extraction, utilizing methyl isobutyl ketone (MIBK) or other suitable organic solvents will be studied for relative efficiency of overall removal of organic material (TOC) as well as for the removal of selected specific organic and inorganic compounds. MIBK will be utilized initially because of its low water solubility, polarity and boiling point. Specific compounds to be monitored will be selected based on their concentration in the aqueous phase and their predicted partition coefficient under the conditions of the solvent extraction process. The number of stages of solvent extraction will be based on the actual partition coefficients obtained.

c. Process Sequence

An evaluation will be made of the most appropriate process sequence of the two physical-chemical pretreatment methods. Gas stripping followed by solvent extraction or vice versa will be compared to determine which sequence is more efficient in reducing the concentration of both NH_3 and organic components in the raw wastewater.

d. Pretreatment Process Development

Based on the data obtained in Phase II, Parts a, b, and c, a pretreatment system will be conceived and constructed to pretreat the coal gasification wastewater prior to its use as a substrate for biological treatment during the remainder of the study.

e. Solvent Recovery

A companion study will be initiated to determine the practicality and economic feasibility of recovering the solvent used by simple or fractional distillation procedures.

Phase III: Biological Treatment Processes

This phase of the study will examine the applicability of utilizing anaerobic filters in combination with aerobic nitrification to treat both raw and pretreated coal gasification wastewaters. The effort will be accomplished in several steps and will employ several duplicate reactor systems in order to provide flexibility of operation and minimize reacclimation times required when inhibitory or toxic loading limits are reached.

Three complete treatment systems will be employed. Each system will consist of an anaerobic filter packed with Raschig Rings followed in series by an anaerobic filter packed with granular activated carbon. Effluent polishing will be accomplished in each case with an aerobic nitrification system consisting of either an aeration basin and a clarifier or a rotating biological contact (RBC) unit. The addition of powdered activated carbon (DuPont's PACT Process) to the aeration basin will also be considered.

The wastewater treatability study will be conducted in four stages including:

a. Preliminary Acclimation;

b. System Operation and Evaluation under Inhibitory and/or Toxic Loadings;

c. Evaluation of Recirculation Rate of the Fluidized Activated Carbon Column at Less than Inhibitory or Toxic Loadings; and,

d. Evaluation of System Operation at Minimum Energy Input.

Initially all three treatment systems will be employed in the study but only two systems will be required in Stages c and d.

a. Preliminary Acclimation

All three systems will be initially acclimated utilizing raw wastewater and a nutrient supplemented buffer as a diluent for the raw wastewater. Nutrient supplementation will be based on the initial analysis of the raw wastewater. An additional source of easily biodegradable carbon (i.e., glucose) will be added to the system in order to establish a viable anaerobic microbial population as

rapidly as possible. The anaerobic columns will be seeded with a mixture of digested sludge from a local municipal anaerobic sludge digester and a sludge from an anaerobic system which is currently being operated on a phenolic substrate.

The combined flow rates of the raw wastewater and buffer-nutrient diluent will be adjusted to provide a 12-hour hydraulic retention time in each anaerobic column or a total 24-hour hydraulic retention time in the two column system. Initially, it is anticipated that the raw wastewater feed will be diluted approximately 20:1. As the microbial population becomes established, the concentration of the organic supplement (glucose) will be decreased and the dilution ratio of wastewater to buffer-nutrient diluent will also be decreased. This process will continue until the concentration of organic supplement is zero and the dilution of the raw wastewater feed substrate has been adjusted to give 1000 mg/l TOC in the column feed.

As soon as the pretreatment scheme is finalized and pretreated wastewater becomes available on a continuous basis, one of the acclimated systems will be operated with pretreated wastewater, diluted with the buffer-nutrient diluent. The initial dilution ratio for the system being operated on pretreated wastewater will be based on the efficiency of the pretreatment scheme and the resulting TOC and NH_3 concentrations in the pretreated wastewater.

The recirculation rate for all three systems will be adjusted initially to give a 20 percent carbon bed expansion and will remain at this value until Stage c when recirculation rate studies will be conducted.

The nitrification systems will be operated with a fixed hydraulic retention time of three to six days and apparent sludge ages of 40 to 60 days during the preliminary acclimation. The system will be monitored for alkalinity, TOC, NH_3, NO_2^-, NO_3^- and solids. Alkalinity will be supplemented by use of Na_2CO_3 addition to maintain the pH in the optimum range of 7.8 to 8.2 for nitrifying conditions. Process configurations and modifications will involve sludge recycle and possible use of a rotating biological contact unit or addition of powdered activated carbon with

denitrification depending upon NH_3 concentrations present in the influent to the nitrification system.

b. System Operation and Evaluation with Loadings to Inhibitory and/or Toxic Levels

After the systems have been acclimated to a wastewater substrate loading of approximately 1,000mg/1 TOC (10% wastewater dilution), they will be allowed to come to a pseudo steady state at this loading. Pseudo steady state will be defined as a relatively constant gas production rate and composition and a relatively constant TOC and/or COD removal across the system. At this steady state condition, the system will be evaluated for overall efficiency in terms of both gross and specific parameters. Once this evaluation has been made, the loading on the system will be increased over a short time span (approximately five to ten days) until the loading on the system has been increased by 50 percent.

The two systems being fed raw wastewater will be operated in such a fashion that one of the systems will be operating at a lower loading rate than the other. (See Figure 1).

The performance of the systems will be then evaluated at the new wastewater loading when steady state has been achieved. Once again the loading on the systems will be increased by 50 percent and the systems evaluated when they have reached steady state. This process will be continued until the system receiving the highest raw wastewater loading exhibits either inhibition of biological activity or toxicity as evidenced by decreasing efficiency in treatment capability and/or gas production. An attempt will also be made to assess recovery potentials by loading manipulation and/or feasible environmental adjustments.

It is anticipated that the unit being fed with pretreated wastewater and the lower loading of raw wastewater will still be functioning properly when the first system fails at a higher loading. The loading on the system being fed the lower concentration of raw wastewater will be then maintained at that level to permit the initiation of recycle studies. However, the unit being fed pretreated

wastewater will continue to receive increased loadings and performance evaluations until it is affected by inhibition and/or toxicity.

The unit which showed initial inhibition and/or toxicity (See Figure 1) will be reacclimated to pretreated wastewater and will also be used to study the effect of recirculation rate on system performance using the pretreated wastewater.

c. Evaluation of Recirculation Rate at Less than Inhibitory or Toxic Loadings

The two systems, one being operated on raw wastewater and the other on pretreated wastewater at less than inhibitory or toxic loadings, will be utilized to study the effect of recirculation rates on system performance. The two systems will be operated at that loading rate, but the recirculation rate will be reduced in incremental amounts. The systems will then be allowed to come to steady state and the treatment efficiency will be assessed in terms of gas production and composition as well as removal efficiencies of both gross parameters and specific compounds.

During these investigations, recirculation rates will be adjusted to give the following bed expansions for the activated carbon columns: 20 percent - the initial value as used in previous evaluations, 15 percent, 10 percent, and 5 percent.

d. Evaluation of System Performance at Minimum Energy Input

The system operation which provides the minimum energy input but still allows for reliable operation without gas binding or other operational problems will be determined. This evaluation will provide a basis for determining the most economically efficient system configuration and operating condition.

Phase IV: Assessment of overall Operating Characteristics

The project final report will contain all data collected in the first three phases for the overall operating characteristics of anaerobic filters and polishing treatment for coal gasification wastewater.

In addition, the final report will contain summaries of general design and operating criteria for such systems including the effect of wastewater pretreatment and/or recirculation.

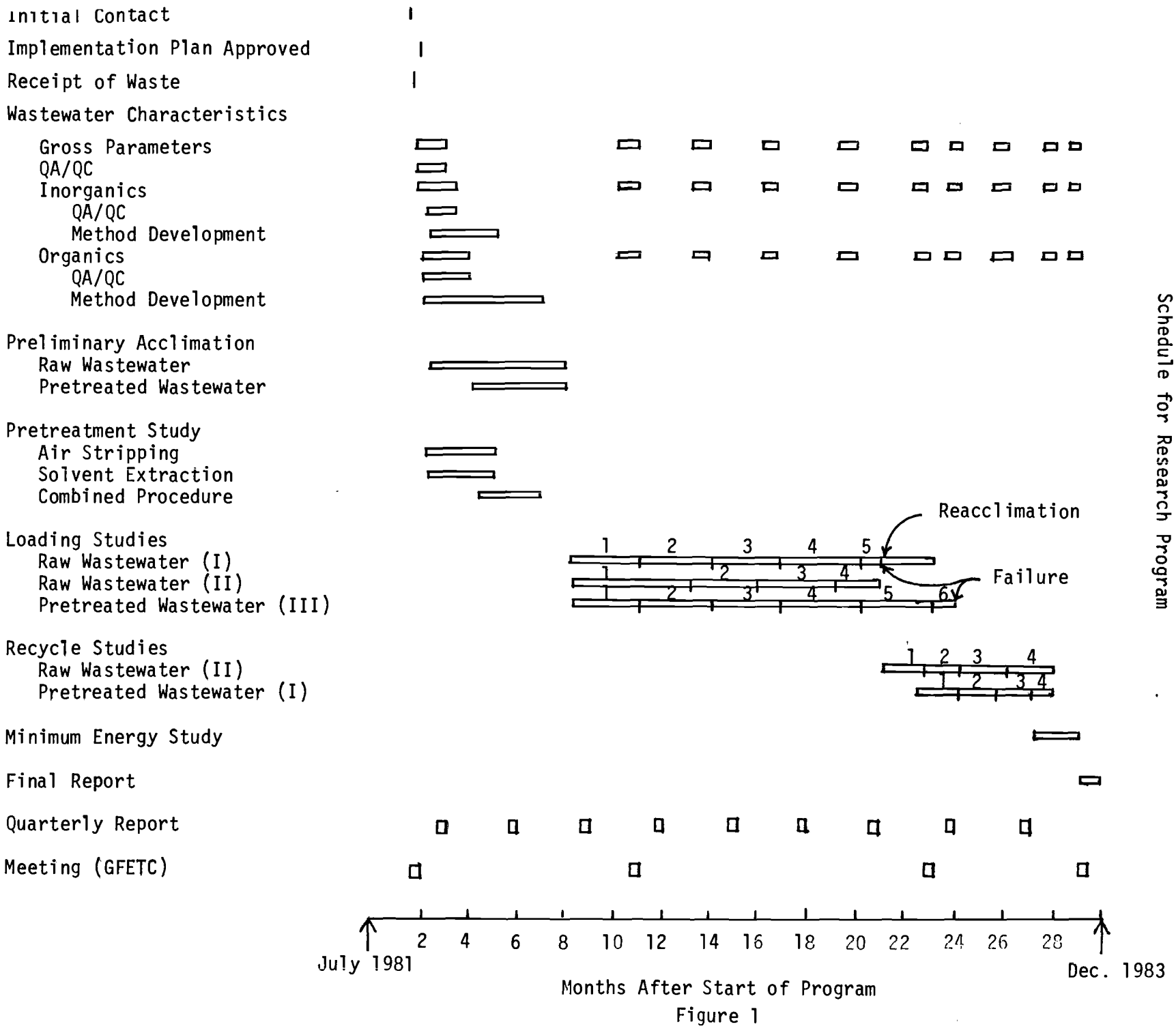
III. PROCESS ALTERNATIVES

Although not all possible problems and their solutions can be anticipated, some projections of possible treatment problems can be made and solutions for these problems suggested. For example, if toxicity and or inhibition is due to inorganic species such as S^{-2}, SCN^-, or CN^-, an additional pretreatment step could be incorporated to remove or reduce the concentration of one of more of these species. This step might consist of precipitation of S^{-2} by addition of a metal ion such as Fe^{+2} or complexation of CN^- by similar treatment. Similarly, several process schemes and/or treatment steps may be indicated. These alternative processes (see Figure 2) will be suggested and evaluated during the progress of the project and may include such innovations as anaerobic phase separation and previously suggested denitrification.

IV. Progress Reports and Expenditures

In addition to the previously mentioned final technical report, quarterly technical and contract management reports will be submitted according to the schedule given in Figure 1.

Expenditures for the research program are depicted by the solid line in Figure 3. As actual expenditures occur a dashed line will be plotted in Figure 3 to indicate the financial progress of the project during each reporting period.


Initial Contact
Implementation Plan Approved
Receipt of Waste
Wastewater Characteristics
Gross Parameters
QA/QC
Inorganics
QA/QC
Method Development
Organics
QA/QC
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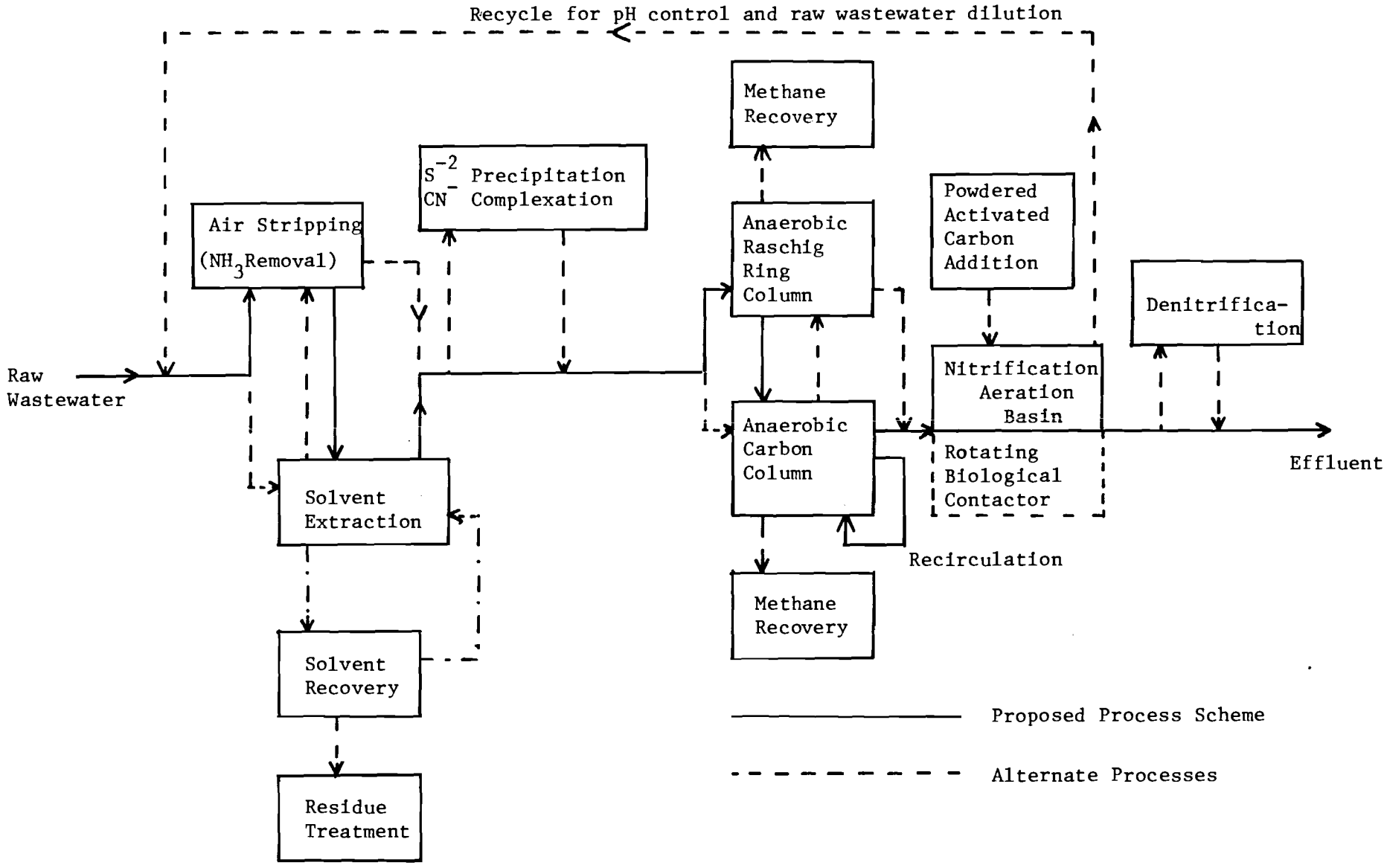
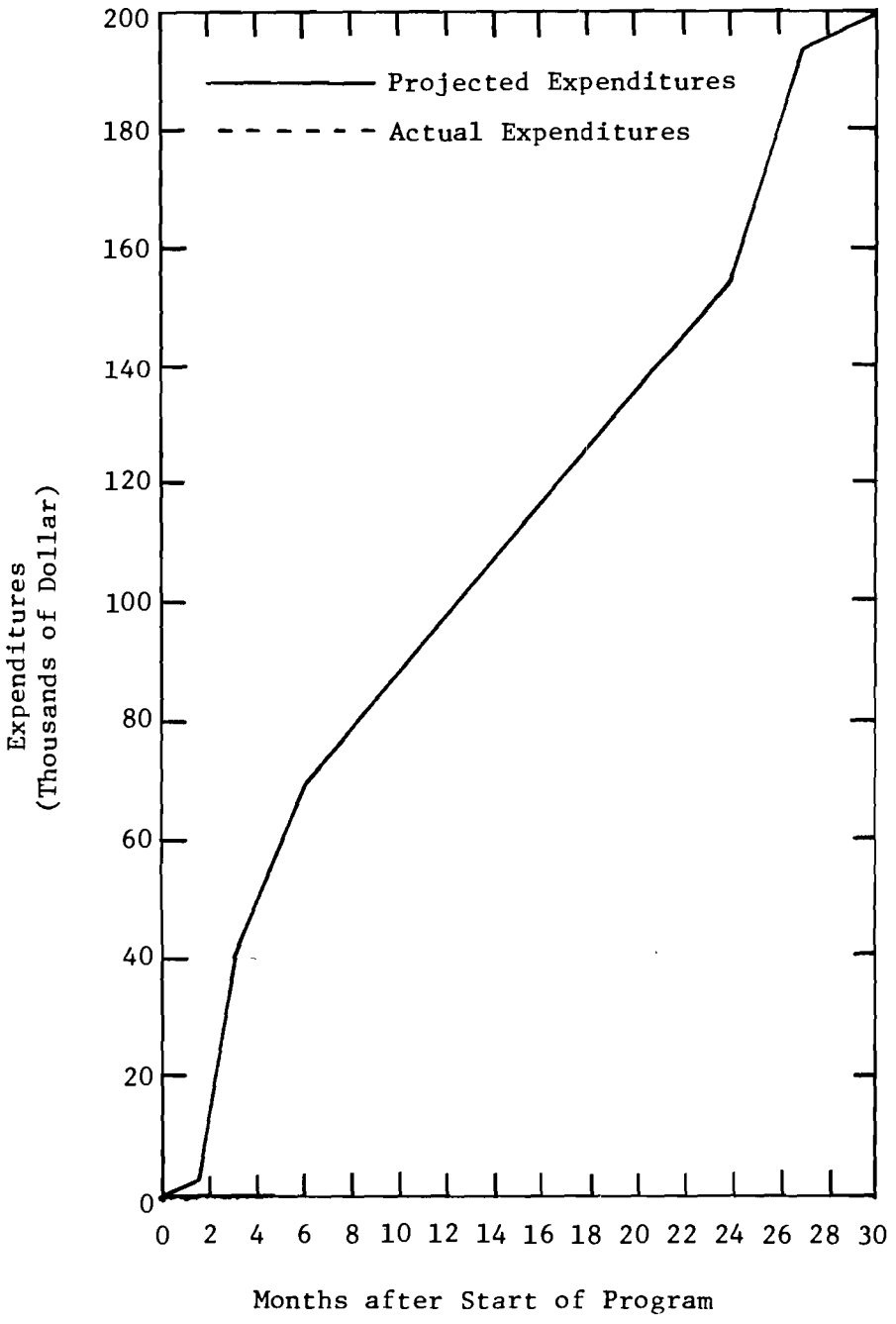
Raw Wastewater
Pretreated Wastewater
Pretreatment Study
Air Stripping
Solvent Extraction
Combined Procedure
Loading Studies
Raw Wastewater (I)
Raw Wastewater (II)
Pretreated Wastewater (III)
Reacclimation
Failure
Recycle Studies
Raw Wastewater (II)
Pretreated Wastewater (I)
Minimum Energy Study
Final Report
Quarterly Report
Meeting (GFETC)
TASK
Schedule for Research Program
July 1981
Dec. 1983
Months After Start of Program

Figure 1



Flow Chart of Treatment Alternatives

Figure 2



Projected Expenditures for DOE Contract No. DE-AC18-81FC10297

Figure 3

Coal Gasification Wastewater
Sample No. RA-87-
12-4-80
1000

Parameter	Value (mg/1 except pH)
pH	8.2
TC	14,500
IC	2,600
TOC	11,900
COD (unfiltered)	26,900
TS	3,670
% volatile	84.7
% fixed	15.2

SCEGIT 86-109

DOE/

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Draft Final Report

By
Wendall H. Cross

July 21, 1986

Work Performed Under Contract No. DE-AC21-81FC10297

Georgia Institute of Technology
Atlanta, Georgia

DOE/

ANAEROBIC TREATMENT OF GASIFIER EFFLUENTS

Draft Final Report
July 1, 1982 - August 31, 1986

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July , 1986

Worked Performed Under Contract No. DE-AC21-81FC10297

Prepared for
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ABSTRACT

Studies have been conducted to determine the biological treatability of coal gasification effluent for removal of organic carbon and ammonia. The treatment system consisted of a anaerobic activated carbon filter for organic carbon removal follwed by a single stage nitrification system followed by a biological denitrification reactor. Dilute (10%) wastewater was successfully treated over an extended period of time.

Attempts to utilize the anaerobic system to treat solvent extracted ammonia stripped coal gasification effluent to remove substituted hydantoins was of limited success.

Batch inhibition studies showed substituted pyridines as the primary inhibitory compounds in the raw wastewater.

Carbon adsorption-solvent regeneration for hydantoin removal did not appear to be a viable treatment alternative due to low adsorption capacities and incomplete regeneration of the activated carbon.

INTRODUCTION

Coal gasification is regarded as one of the promising technologies in alleviating the nation's energy problems caused by decreasing supplies of natural gas and petroleum. However, wastewaters generated from coal gasification contain high concentrations of phenols, cresols and ammonia, and lower amounts of cyanide, thiocyanate, and other trace organic compounds. Pretreatment, i.e., solvent extraction followed by ammonia stripping, is capable of markedly reducing the concentration of phenolic compounds and ammonia. However, there remains in some wastewaters high concentrations of highly water soluble compounds such as substituted hydantoins.

The aerobic activated sludge process has been used to remove organic contaminants from dilute coal gasification wastewaters [1-6]. Most coal conversion technologies incorporate or project the use of aerobic processes as the principle means for treating the residual organic compounds and other impurities present in such wastewater[1]. Such processes are very energy-intensive, with aeration times often exceeding four days. Moreover, instabilities induced by variations in the chemical characteristics of the influent waste stream are often encountered.

In treatability studies conducted on wastewater generated by the Morgantown Energy Research Center fixed-bed coal gasifier, Sack and Bokey[3] observed that major constituents of coal gasification wastewater escape treatment in the activated sludge process even at aeration times exceeding six days. Aromatic amines, thiophenes, and polycyclic hydrocarbons were found to be specially resistant to aerobic treatment while the phenolic content of the treated effluent was invariably in excess of desired levels. Ganczarczyk and Elion[7] obtained similar results from extended aeration treatment of coke plant effluents. Luthy[4] studied a variety of wastewaters generated by coal coking and coal gasification processes and found, with a number of forms of pretreatment, that biological treatment of coal conversion effluents resulted in good removals of biological oxygen demand (BOD), chemical oxygen demand (COD), phenols, ammonia-nitrogen, and cyanogen-nitrogen using hydraulic retention times of 2-20 days. However, microbial yields were relatively low, which was attributed to inhibitory constituents in the wastewater. In a similar study, Stamoudis[8] obtained comparable results using hydraulic retention times of two to nine days.

Inhibition of aerobic treatment of coal conversion wastewaters is believed to be due to several constituents present in these wastewaters. Thiocyanate, which is poorly degraded in aerobic biological treatment, exhibits an inhibitory effect on the aerobic biodegradation of phenol[8], while cyanide, thiocyanate, and phenol have been observed to inhibit nitrification of ammonia. Juntgen and Klein[9] have studied the coinhibition of phenol, thiocyanate, and ammonia during aerobic treatment.

In cross acclimation studies of the treatment of petrochemical wastes in a conventional anaerobic filter, Chou[10] found that the anaerobic environment provided rather rapid acclimation to shock loadings of phenol, catechol, resorcinol, nitrobenzene, and cyanide. Van Velsen[11] demonstrated with treatment of piggery wastes that anaerobic organisms could function efficiently at ammonia concentrations exceeding 6000 mg/L and pH levels of 8. Lettinga[12] demonstrated that these systems also acclimated rapidly to cyanide.

The feasibility of using anaerobic systems for the treatment of phenol as an alternative to conventional aerobic biological systems has been reported by Hobson et al.[13]. The biokinetics of anaerobic phenol degradation has been studied by Neufeld[14], and Chemielowski[15] has performed specific kinetic research on the anaerobic decomposition of phenol. Healy and Young[16] have demonstrated the process of degradation of phenol and catechol by methanogenic population of bacteria. The anaerobic biodegradability of phenol and catechol has also been confirmed by Khan et al.[17] and Suidan et al.[18]. However, most of these anaerobic biological studies on degradation of phenolic substances involved single synthetic substrates of relatively low concentration. The treatment process used in this study combines the advantages of the energy-efficient anaerobic filter process developed by Young and McCarty[19] and later modified by Chian and DeWalle[20] with recirculation and the adsorptive capacity of activated carbon for the extended detention of less readily biodegradable compounds as originally reported by Khan et al.[17] for the anaerobic degradation of phenols. Recent work by Suidan[21-22] has shown the applicability of anaerobic filters for treating coke wastewaters.

Activated carbon is often used as a contact medium for biological treatment systems since it has the excellent characteristics of being light-weight, having a large surface area, a large void volume, and surface properties that are conducive to the growth of microorganisms . The activated carbon may also adsorb inhibitors to microbe metabolism which would allow the biological treatment process to continue even though inhibitory agents are present in the waste stream. In this regard, it is particularly useful as a medium for anaerobic filters since anaerobic treatment processes are relatively sensitive to inhibition. Results from anaerobic filters studied as a treatment alternative for the water quench waste stream from a pilot-scale coal gasifier operated by the University of North Dakota Energy Research Center (UNDERC) are the basis for this report.

The UNDERC gasifier is in a commercial dry-ash, slagging fixed-bed configuration[23]. Coal is gravity fed from hoppers at the top of the gasifier, and is combusted and gasified by a countercurrent flow of hot gases. An oxygen/steam mixture is introduced at four tuyeres positioned above the hearth. Ashes exit the bottom of the furnace while hot product gases, devolitalization products and steam exit the top of the gasifier at approximately 325°F. The hot gases enter a spray cooler or water quenching vessel where recycled gas liquors mixing with the gas stream removes soluble gases and devolitalization products. The soluble gases removed include NH_3, CO_2, HCN, and H_2S while the devolitalization products include tars, oils, and water vapor. The product gas then is processed through an overhead gas cooler where additional light oils and water vapor are removed.

The wastewater streams in the gasification process are the gas liquors from the spray cooler and light oils and water vapor from the overhead gas cooler. Both streams are sent to a tar/oil/water separator where oils and tar are gravity separated.

Wastewater pretreatment is accomplished by filtration to remove residual tars and passed through a solvent extraction column for the removal of phenol. The solvent used is diisopropyl ether. The solvent-extracted wastewater is then heated through a heat exchanger to 190°F to 200°F and introduced to a stripping tower. A counterflow of steam removes ammonia and acid gases from the wastewater.

RESEARCH OBJECTIVES

Objectives of the overall research project included:

1. A study of the treatability of raw GFSFBG effluent using a two stage anaerobic activated carbon filter and determination of maximum loading rates and the effect of recycle rate on treatment performance.

2. Identification of compounds inhibitory and/or toxic to the biological treatment system.

3. Determine the applicability of biological treatment for the removal of ammonia from the anaerobically treated effluent (nitrification-denitrification).

4. Determine the treatability of solvent extracted ammonia stripped wastewater for removal of hydantoins using anaerobic activated carbon filters.

5. Determine the adsorption capacity of granular activated carbon for hydantoins.

6. Investigate the solvent regeneration of granular activated carbon saturated with hydantoins.

MATERIALS AND METHODS

Wastewater Sources

All wastewater was produced at the Grand Forks Energy Technology Center (GFETC) and shipped to the Georgia Institute of Technology (GIT) via refrigerated trucks. Upon receipt at GIT the wastewater was stored frozen in five gallon plastic containers. Individual containers were thawed as needed, composited in fifty gallon batches, diluted and used in the project. Two different batches of gasifier effluent were used in the study. These were designated by GFETC as RA-52 and RA-87. A separate batch of pretreated (solvent extracted-ammonia stripped) wastewater was utilized for the feasibility study of the anaerobic treatment of hydantoins and the adsorption-solvent regeneration of granular activated carbon.

Results of the analysis of the raw gasifier wastewater and the pretreated wastewater are presented in Appendix A Tables 1, 2 and 3.

Biological Treatment Systems and Carbon Adsorption-Regeneration System

Schematic diagrams, physical dimension, and operating characteristics of all systems used in the study are given in Appendix B.

Analytical Methods

Specific methods of analysis used for the evaluation of all samples are given in Appendix C. In general all samples were filtered through a 0.45 μ membrane filter prior to analysis.

Feed Substrate. The feed substrate employed in this study was an aqueous solution of coal gasification wastewater having a concentration up to 10% coal gasification wastewater.

During the initial acclimation phase, glucose was also added to one system to provide a readily available carbon source for bacterial growth. Unlike the procedure reported by Khan at al.[17], no vitamins or trace metals were added but a mixture of sodium and potassium phosphates were included to supplement the wastewater with phosphorus.

Process Monitoring. Daily checks of pump flow rates, carbon bed expansion, feed reservoir volume, pH, and gas production were made for each system. In addition, weekly determination of total organic carbon (TOC), COD, oxidation reduction potential (ORP), alkalinity, total volatile acids, phenol, and gas composition were performed on influents and effluents from the anaerobic systems in order to assess the performance of each unit in terms of removal efficiency of organic contaminants and the production and conversion of specific compounds, such as organic acids and phenol.

RESULTS AND DISCUSSION

Anaerobic Filters

The four pilot-scale two-stage anaerobic Raschig ring and granular activated carbon filter systems used in this study were operated at empty-bed hydraulic retention times of 24 hour in each column. The Raschig ring packed fixed-bed reactor was operated in a plug-flow mode, whereas the granular activated carbon reactor was operated in a fluidized (well mixed) mode. The latter was accomplished by means of effluent recycle at an upflow rate of 5 gpm/ft^2 (13.3 $m^3/m^2/h$). As indicated in Table 4, systems I and II were started on Day 0 and operated approximately one year; Systems III and IV were started on Days 87 and 380 respectively (Table 5).

Phase I - Acclimation

During the 147 days of phase I, the first-stage Raschig ring packed column was seeded with approximately 4 L of settled digested sludge (ca.5-6%) solids collected from a local sewage treatment plant (R. M. Clayton Plant, Atlanta, GA). The procedure for seeding the Raschig ring packed column was based on previous experience with difficulty of acclimation of the fluidized carbon bed without such a seed material. The procedures for acclimating the system receiving coal gasification wastewater are given in Table 4. As shown, the substrates fed to the system were maintained at 1000 mg/L TOC. During this phase of the study, glucose was added to one reactor system to facilitate rapid accumulation of a bacterial population producing methane gas. An increasing concentration of wastewater with a concomitant decrease of the glucose concentration was added to the feed to enhance acclimation of the microorganisms capable of degrading the coal gasification wastewater. The use of this start-up procedure was found to have little effect on the rate of acclimation of the sludge toward degrading coal gasification wastewaters in either system.

Table 4

ANAEROBIC REACTOR FEED COMPOSITION

Phase I	Duration Days	Flow Rate ml/min	System I		System II	
			Wastewater mg/L TOC	Glucose mg/L TOC	Wastewater mg/L TOC	Glucose mg/L TOC
A	1-50	10	500	500	500	500
B	50-70	10	800	0	800	0
C	70-84	7	800	0	700	300
D	84-112	7	1,000	0	700	300
E	112-147	7	1,000	0	800	200
Phase II	147-194	10	1,000	0	1,000	0

Table 5. Start Up of Systems III and IV

System II - Series of one Rashig Ring and one AFAC Filter*
System III - One AFACF with cyclic carbon replacement
System IV - Series of three AFAC Filters

SYSTEM 3				SYSTEM 4			
DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l	DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l
87-133	10	500	500	410-440	5.0	0	1000
134-147	10	400	600	441-455	6.0	0	1000
148-167	10	300	700	456-466	7.5	0	1000
168-195	10	200	800	467-	10.0	0	1000
196-216	10	100	900				
217-	10	0	1000				

*See Cross et al. (1982) for Acclimation Procedure

Phase II - Pseudo-Steady-State Operation

During the 47 days of phase II, both systems were operated under identical conditions with a feed consisting of diluted coal gasification wastewater (ca. 10% raw wastewater) and phosphates. Feed flow rates were maintained at 10 mL/min (14.4 L/d) to each system and the systems were monitored to assess their performance.

Chemical oxygen demand and TOC removals, indicated in Figures 1-4, exhibit similar performance for both systems, with COD removals increasing with time. The COD removals averaged 77.6 and 87.1% for systems I and II, respectively, while corresponding TOC removals averaged 73.0 and 78.1%. Phenol removals, shown in Figures 5 and 6, were in excess of 90% for both systems. Phenol removals decreased somewhat after day 147, when the overall loading on the system increased, and then began increasing again with final effluent concentrations in the range of 20-40 mg/L. Only 10-20% of the phenol was removed in the first-stage Raschig ring column, with the remainder being removed in the second-stage granular activated carbon column.

Removal of cresols has also been monitored during steady-state Operations. Overall removal efficiencies were 99.9 and 99.4% for systems I and II, respectively, with approximately 58% being removed by the Raschig ring column and 41% by the granular activated carbon columns.

Volatile fatty acids concentrations, shown in Figures 7 and 8, indicate fluctuations in concentration during the acclimation period due to changes in loading and other operational stresses imposed on the systems. However, there was an overall decrease in the acid concentrations as the systems became acclimated and more completely converted the acids to methane and carbon dioxide. Levels of total volatile fatty acids in the final effluent were on the order of 100 mg/L.

Gas production, shown in Figures 9 and 10 continued to increase during the acclimation period until rates of 5.7 L methane/day for system I and 3.6 L methane/day for system II were achieved. The quantity of methane being produced by system I was slightly in excess of that calculated from the anaerobic degradation of the influent phenol, while the amount produced by system II was slightly less. However, no correction has been made for conversion of substrate to biomass or for the solubility of methane in water. Approximately 86% of the methane produced was generated by microbial activity within the granular activated carbon columns.

Suspended solids in the effluent of the granular activated carbon columns were on the order to 20 and 40 mg/L for systems I and II, respectively.

CONCLUSIONS

Wastewater from coal gasification processes are amenable to treatment by a two-stage anaerobic filter packed with Raschig rings and granular activated carbon. Results indicate that good removal of the major wastewater constituents were obtainable using a dilute wastewater (ca. 10% raw wastewater) with a total empty-bed retention time of approximately two days. At a loading of 2.5 kg COD/m^3d the two-stage system had removal efficiencies of 87% COD, 78% TOC, 93% phenol, and 99% cresols during pseudo-steady-state

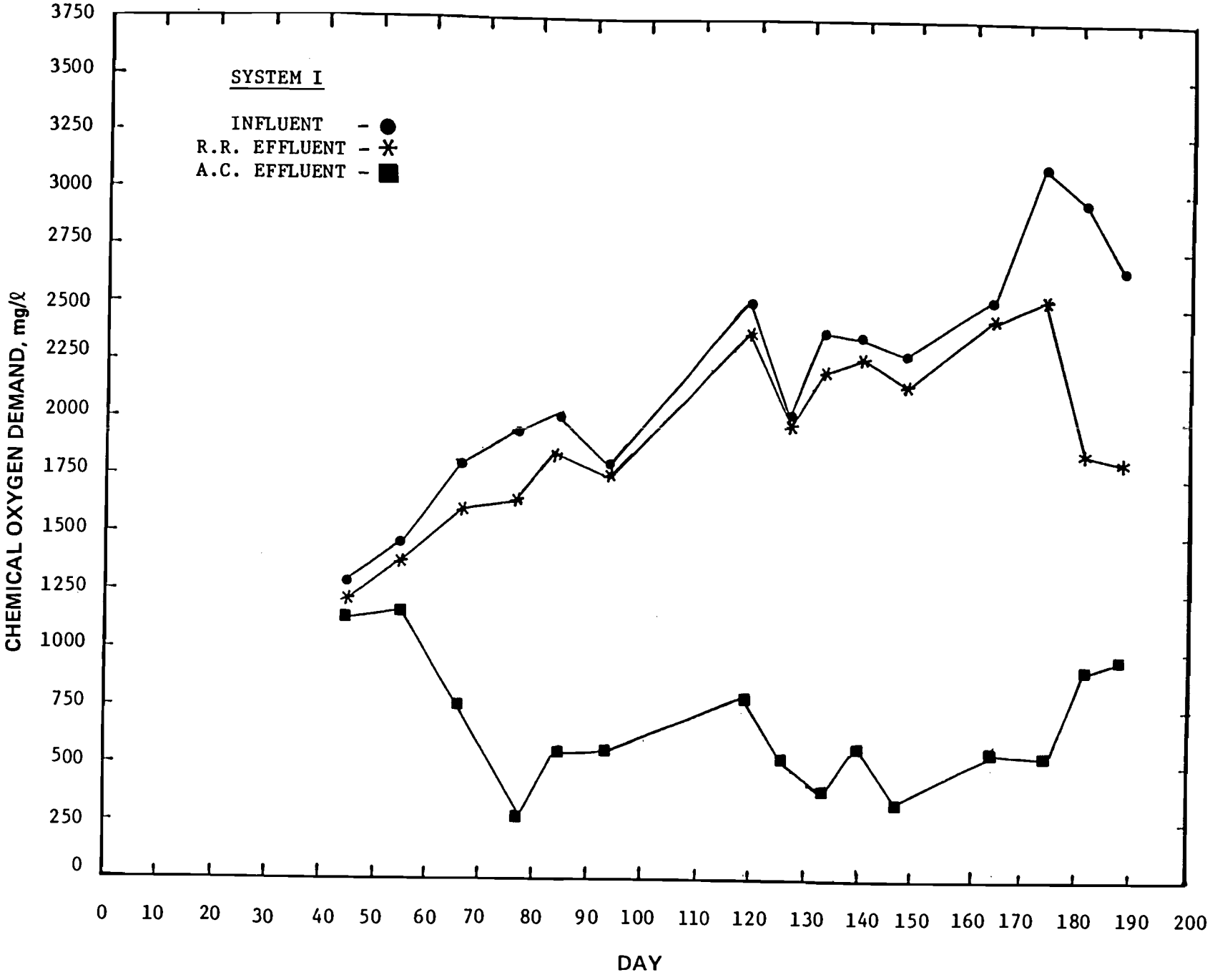

Fig. 1 COD Removal System I.

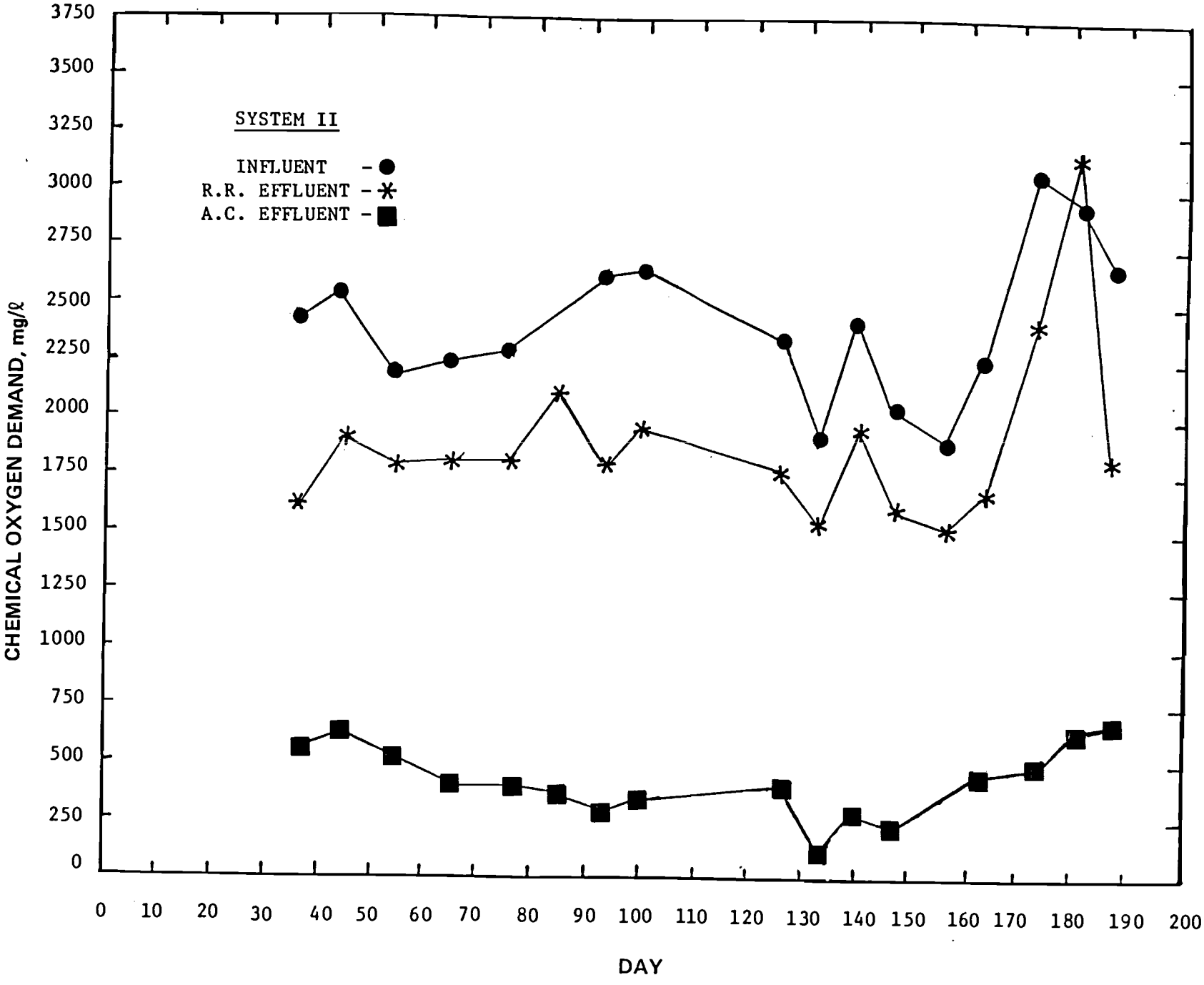

Fig. 2 COD Removal System II.

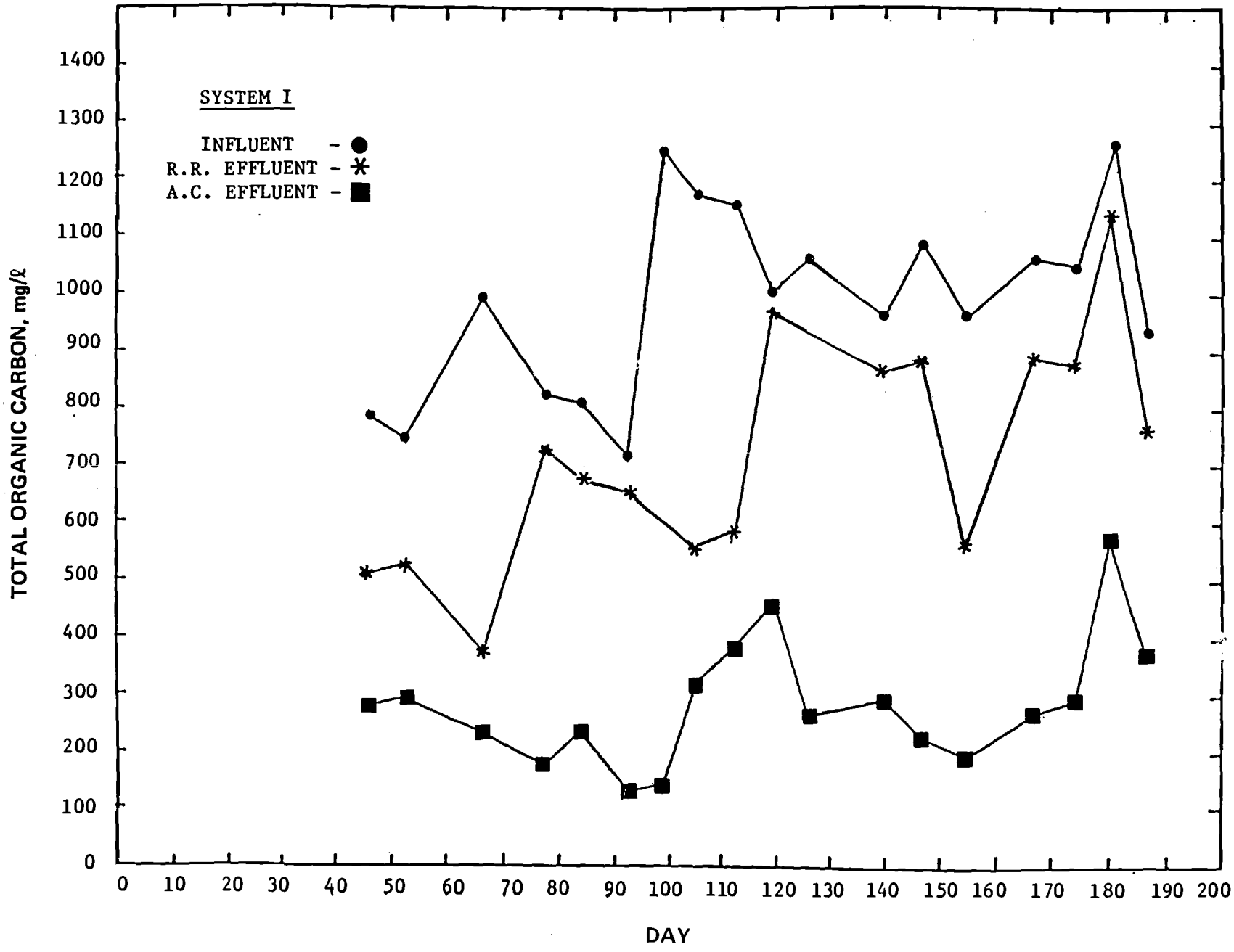

Fig. 3 TOC Removal System I.

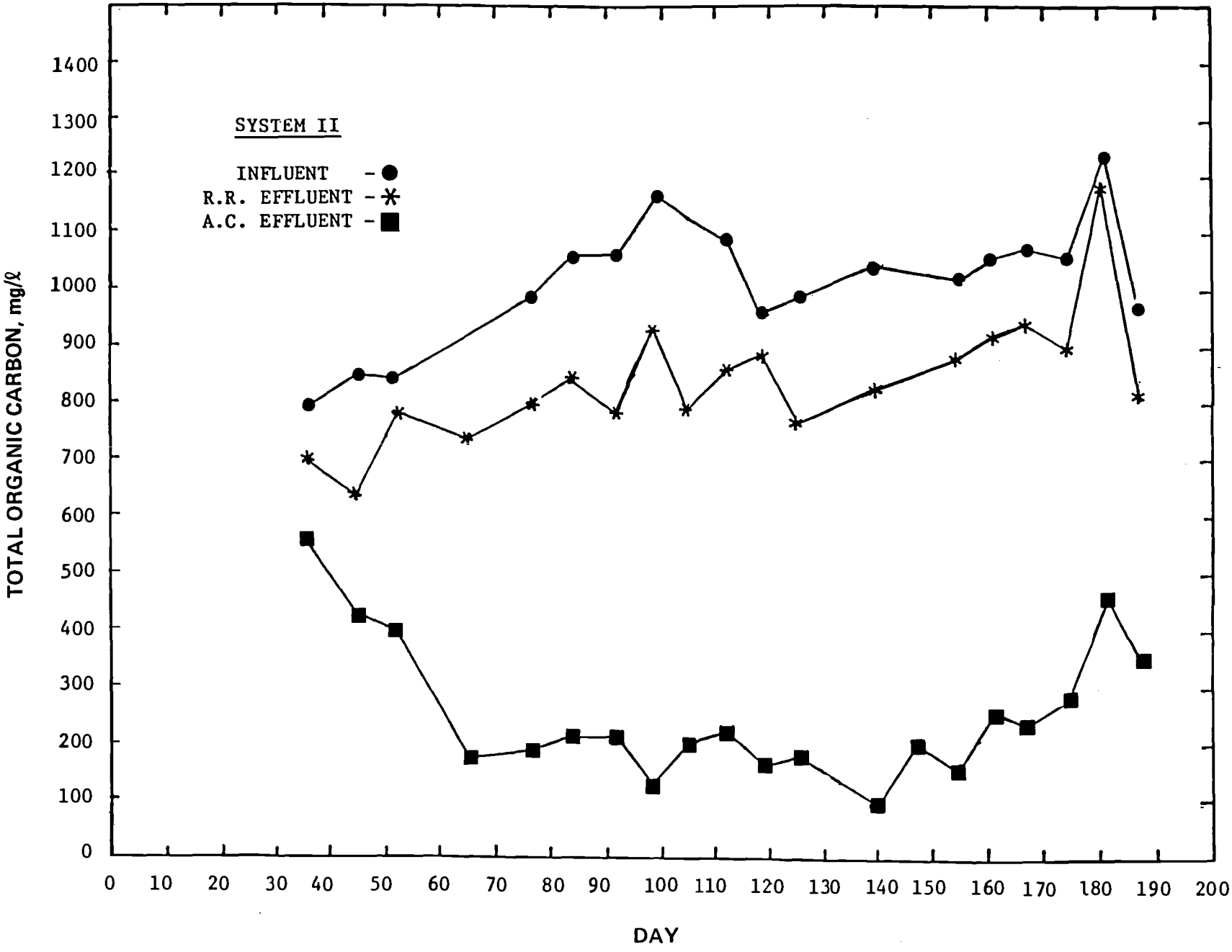

Fig. 4 TOC Removal System II.

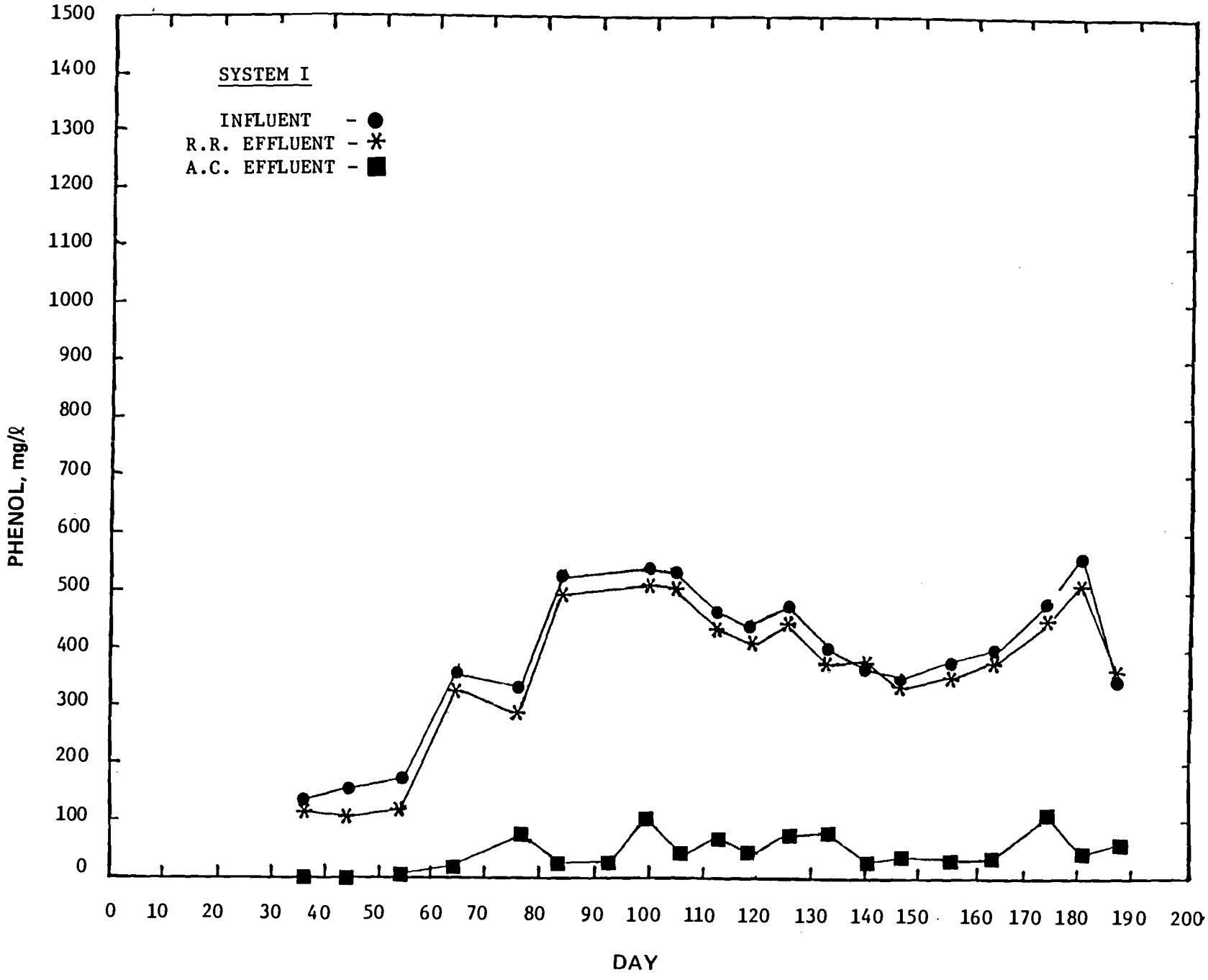

Fig. 5. Phenol Removal System I.

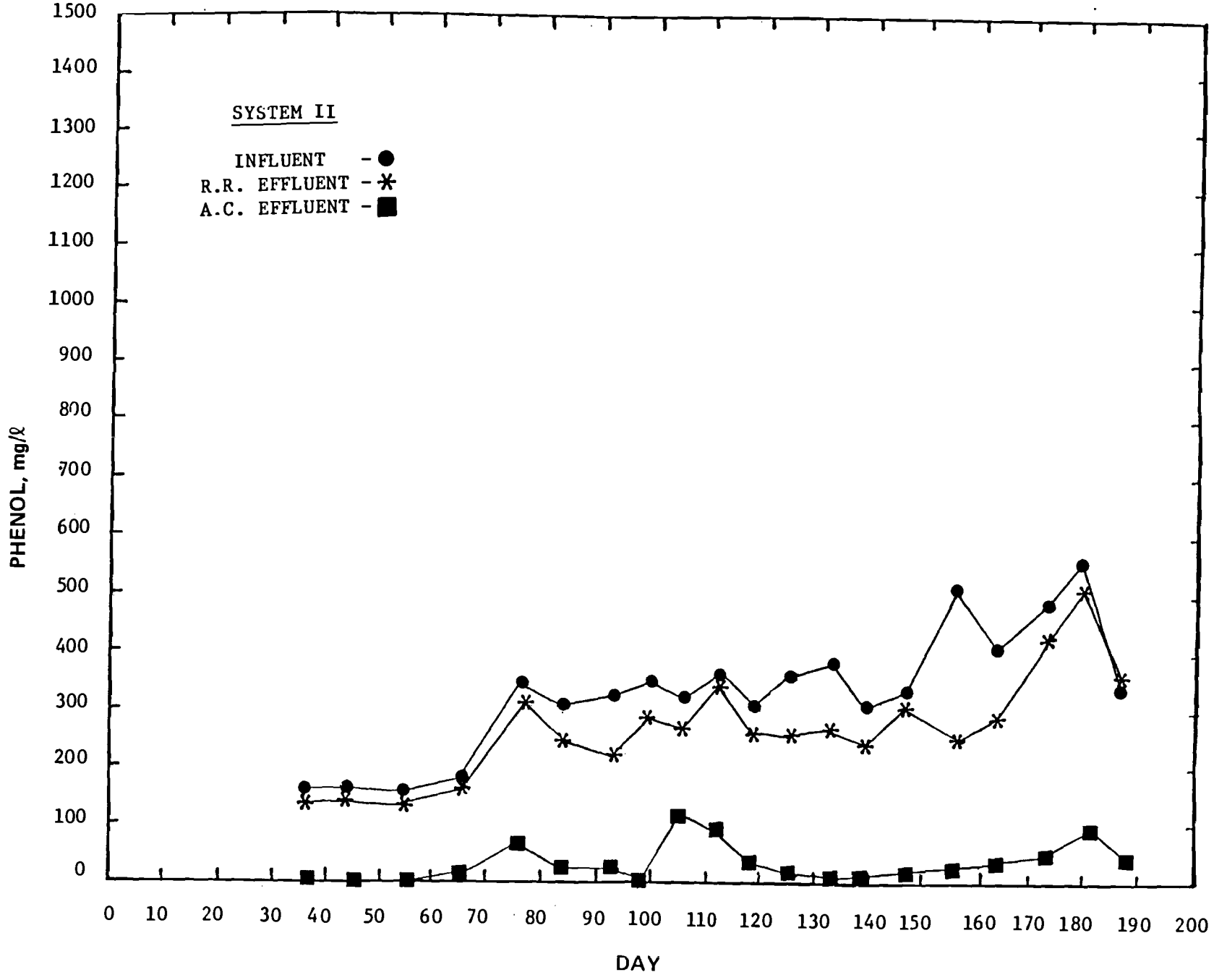

Fig. 6 Phenol Removal System II.

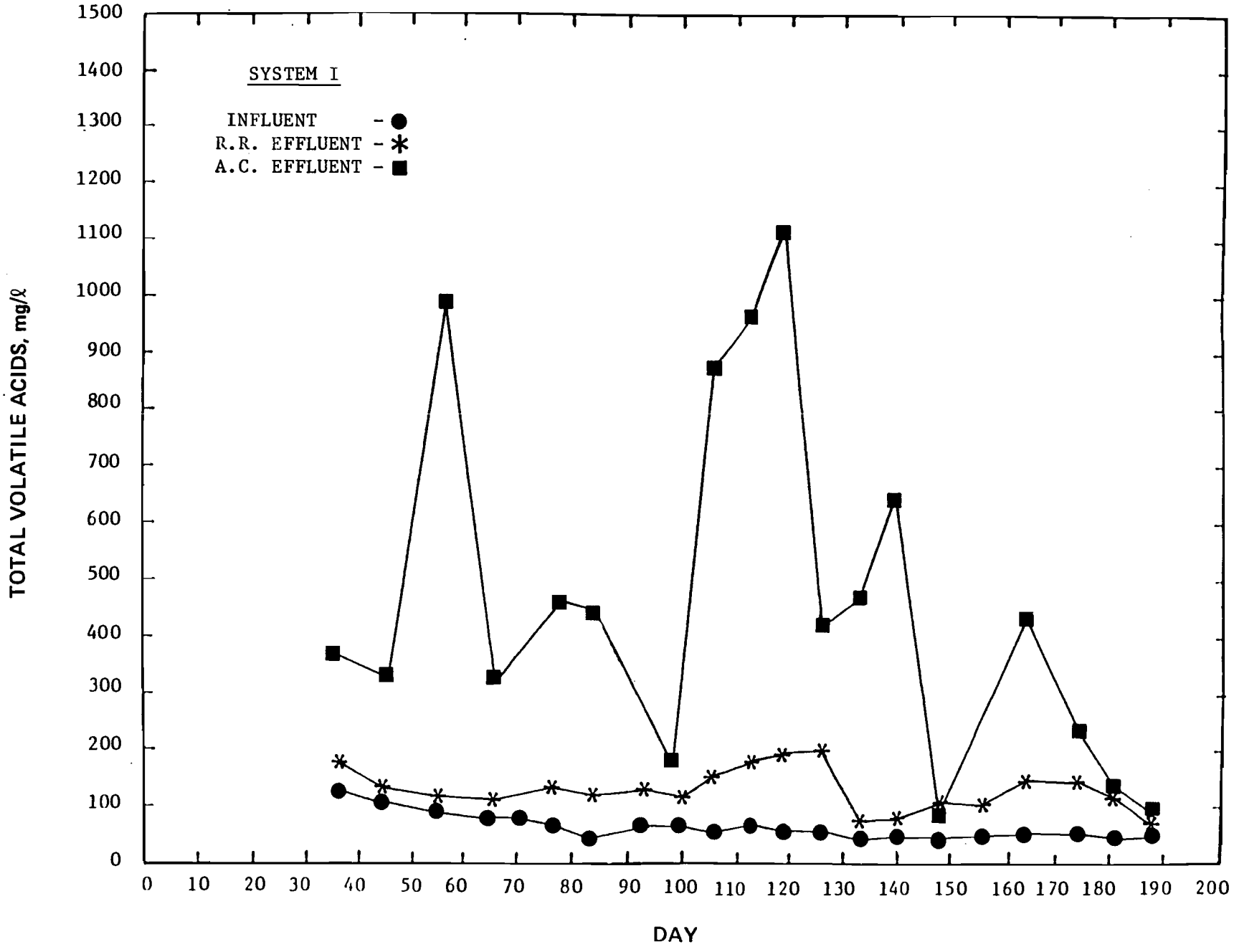

Fig. 7 Total Volatile Acids System I.

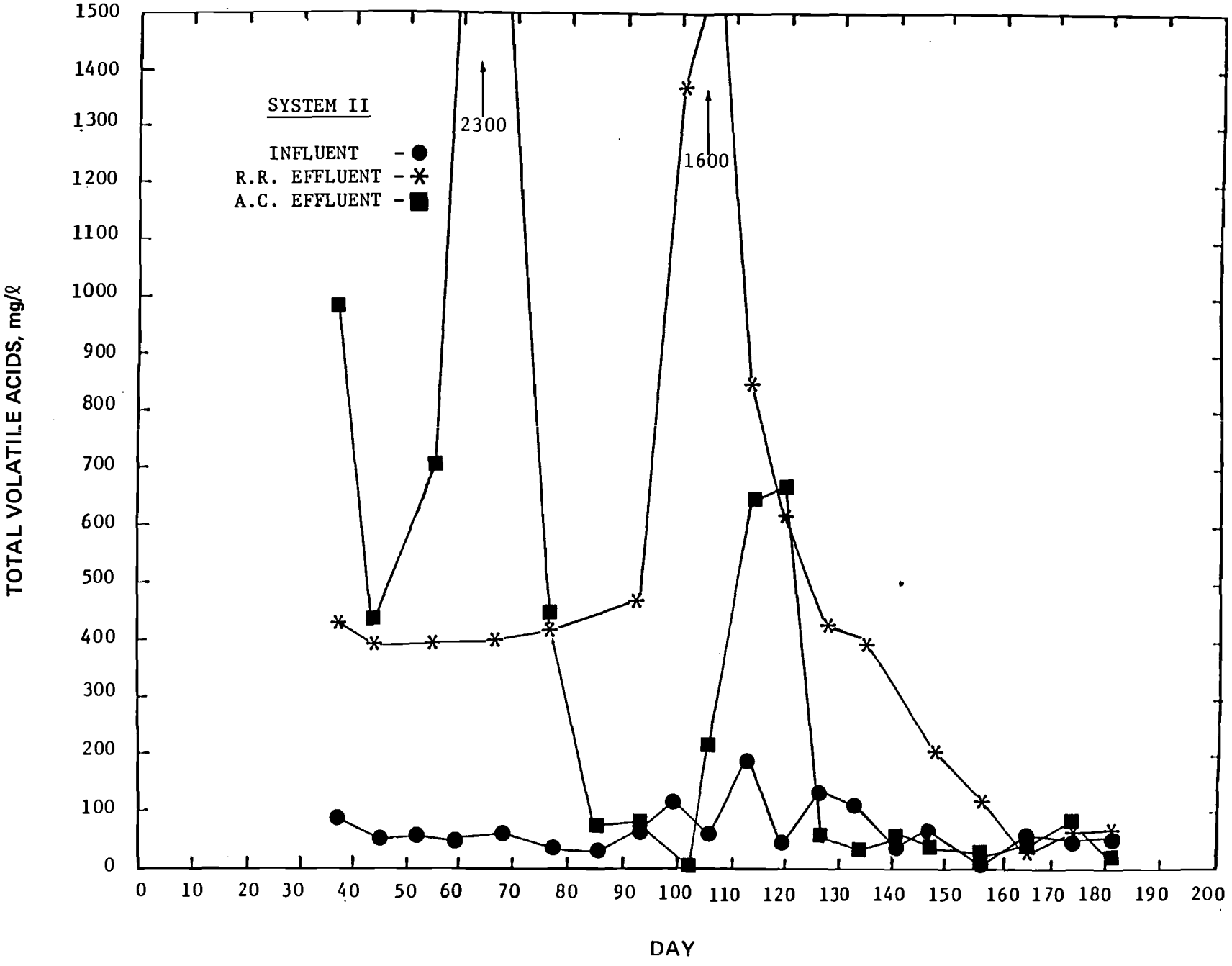

Fig. 8 Total Volatile Acids System II.

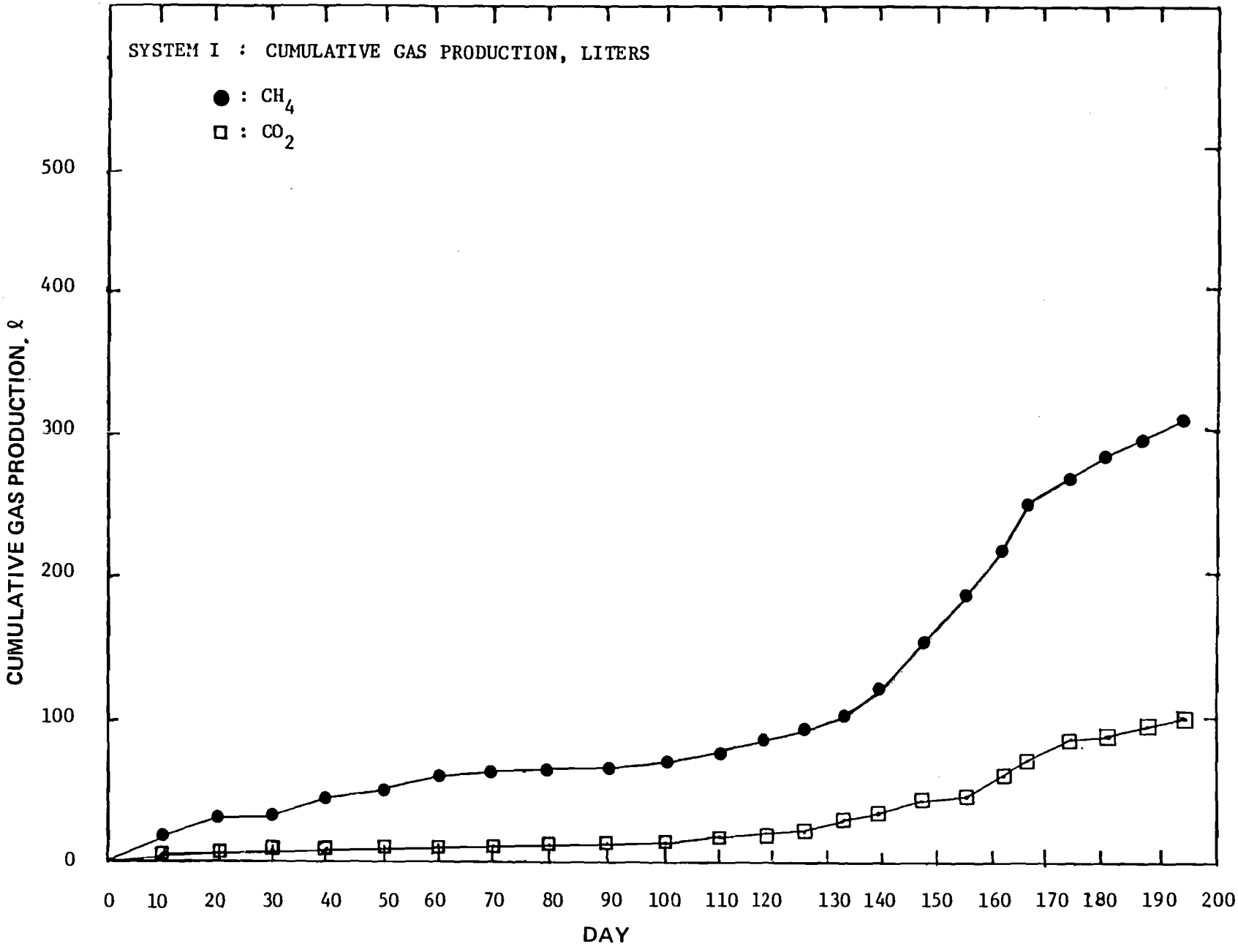

Fig. 9 Gas Production System I.

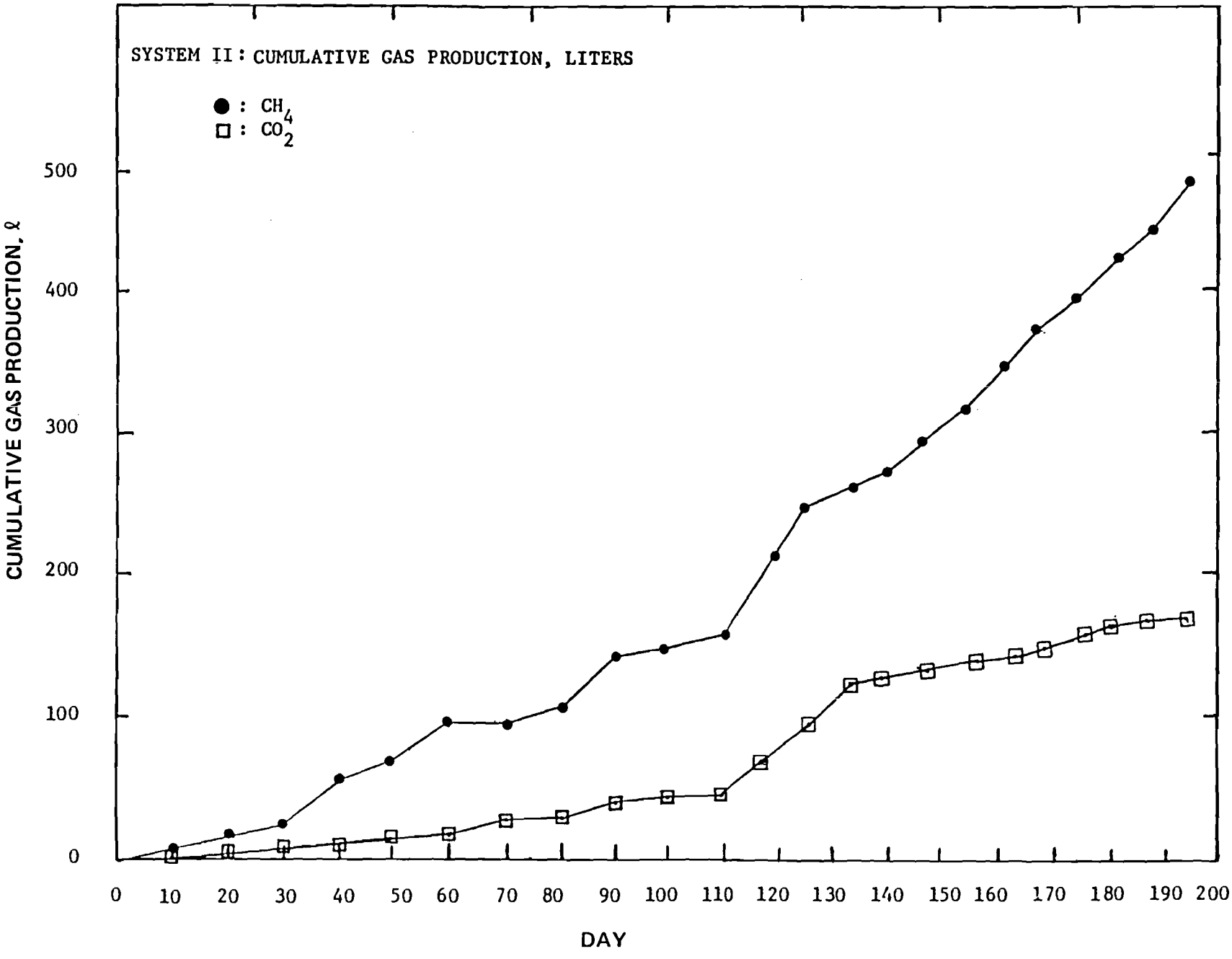

Fig 10 Gas Production System II.

operation. No apparent inhibition was observed under the stated operating conditions.

CARBON REPLACEMENT DUE TO SYSTEM INHIBITION

The study reported herein establishes the relationship between adsorption provided by the activated carbon and the improvement in biological conversion of coal gasification wastewaters. A mutually beneficial relationship has been observed wherein adsorption serves as an in situ pretreatment which promotes conditions suitable for biological growth; the ensuing biological activity extends the life of the carbon via bioregeneration. An understanding of this relationship was considered central to successful operation of the process and for approaching optimum process performance.

Process Inhibition, System II - Carbon Solvent Extraction

Figure 11 shows the variability in performance of system II during its period of operation. On day 195, the influent TOC to the reactor was increased from 1000 mg/L to around 1500 mg/L. Process performance declined rapidly and failed to recover despite attempts at pH control and an ultimate reduction in the organic load. The ensuing search for the cause of process failure led to solvent extraction of the activated carbon with dioxane and dimethylformamide. Subsequent GC/MS, and DS analysis of the solvent extract revealed an accumulation of cresols and C-2 substituted phenols as indicated in Table 6.

Examination of Figure 11 reveals that the beginning of process failure appeared to coincide with carbon saturation as indicated by the almost complete breakthrough of cresols at about day 200. Unfortunately, an increase in loading rate was effected at this same time; therefore it was not possible to clearly distinguish whether the process failed due to overloading, inhibition due to some component remaining in solution in the absence of adsorptive removal, or a combination of the two.

Process Inhibition, System III - Carbon Cycling for in situ Pretreatment

System III was carefully monitored with speculation that an inhibitory pollutant might appear at around the time of carbon saturation. Figure 12 shows a slow but constant decline in process performance following phenol breakthrough around day 125, and becoming appreciably more notable following the beginning of cresol breakthrough at around day 210. Particularly poor performance was observed in system III around days 330 and 440. Figure 12 shows an accumulation of volatile acids under these conditions, which suggests that the methanogens are inhibited first.

Soon after cresol saturation, COD removal efficiencies declined from 70% to around 30%, and gas production ceased. Therefore on day 456 one liter of fresh carbon (10% of the total carbon bed volume) was added to avert reactor failure. Performance of the system in terms of COD, TOC, phenol, and cresol improved immediately, as shown in Figure 13. On day 461 a 10% increase in gas production was noted, but only for a short period of time. Within 10-12 days of carbon addition, the removal efficiencies of the process had declined to their previous unsatisfactory levels. On day 488, a second dose of carbon was added to the reactor by removing 3 L of spent carbon from the reactor and adding 2 L of fresh carbon; returning the carbon bed to its original volume of 10 L.

Removal efficiencies were again improved immediately, and were followed by a large increase in gas production to about 8.4 L per day (70% methane) or

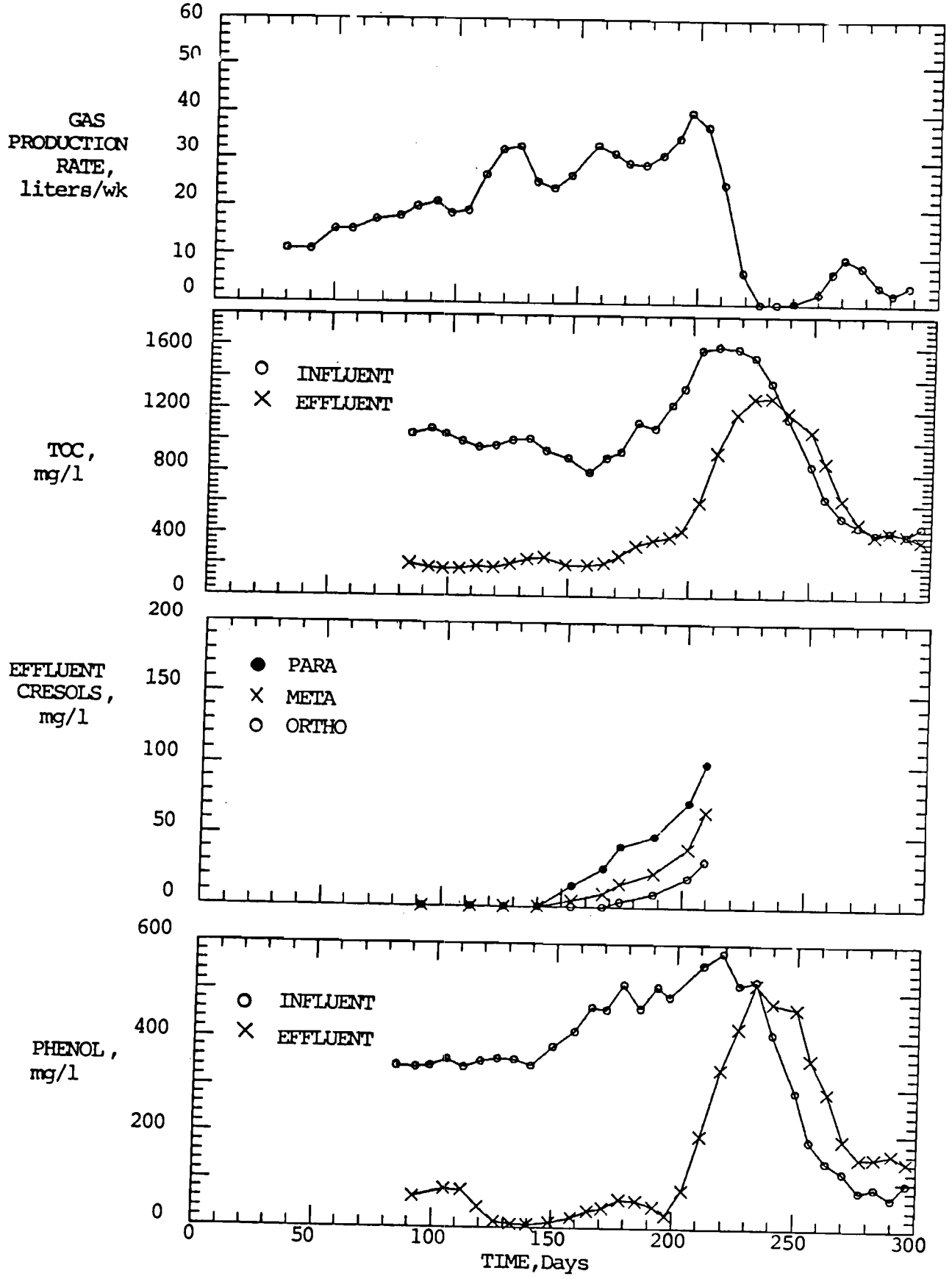

Fig. 11 Performance of System II.

Table 6. Organic Pollutants Extracted From Granular Activated Carbon

Compound	Concentration mg/l
Pyridine	4.6
2-Picoline	3.7
4-Picoline	5.8
Aniline	1.9
Benzonitrile	0.7
2-Methoxyphenol	169.0
2,6-Dimethylphenol	6.8
2,4-Dimethylphenol 2,5-Dimethylphenol	125.0
4-Ethylphenol 3,5-Dimethylphenol	118.0
3-Ethylphenol	9.2
3,4-Dimethylphenol	28.6
3-Methoxyphenol	1.2
4-Methoxyphenol	1.0
2,3,5-Trimethylphenol	3.4
Indole	2.5

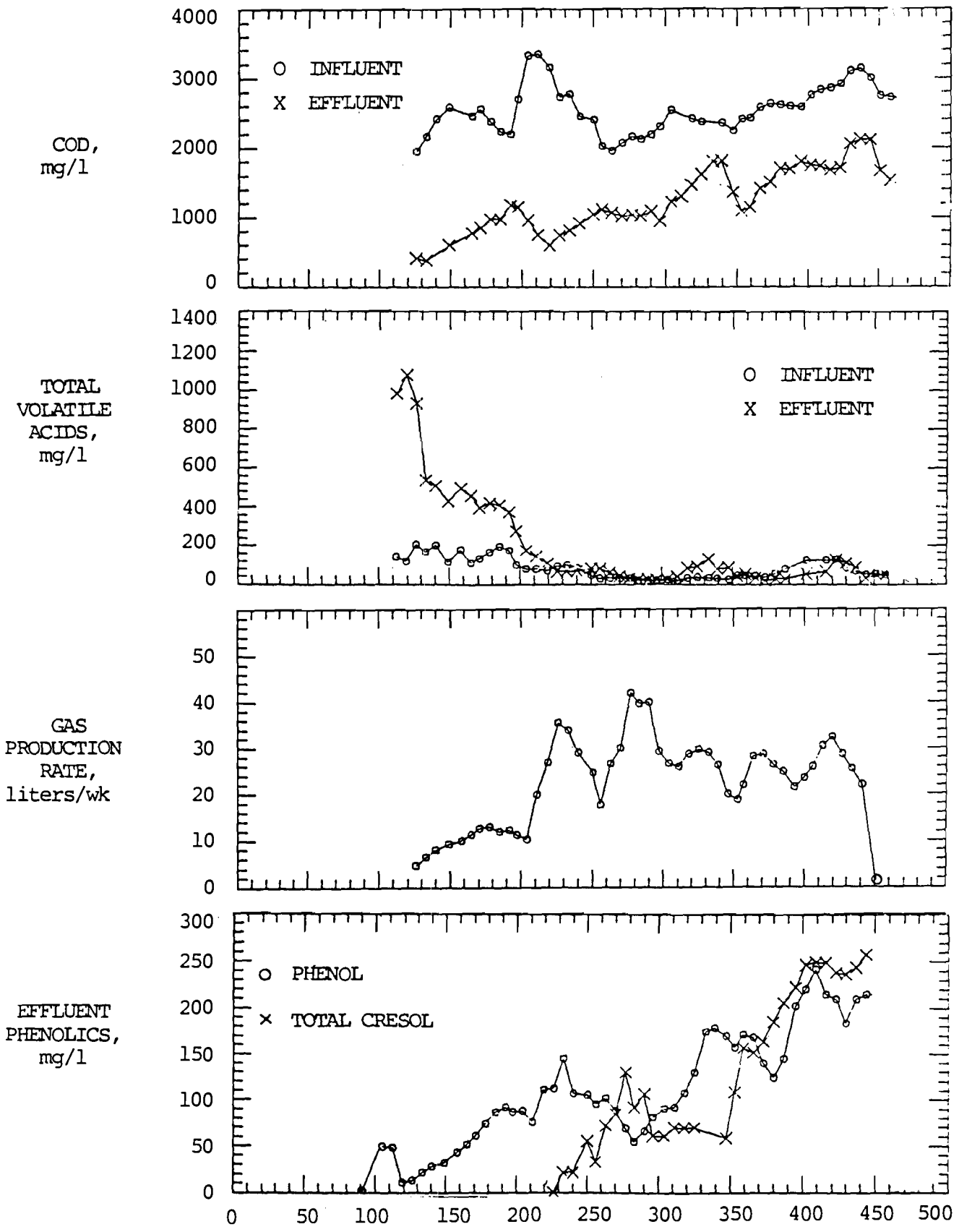

Fig. 12 Performance of System III Prior to Carbon Cycling.

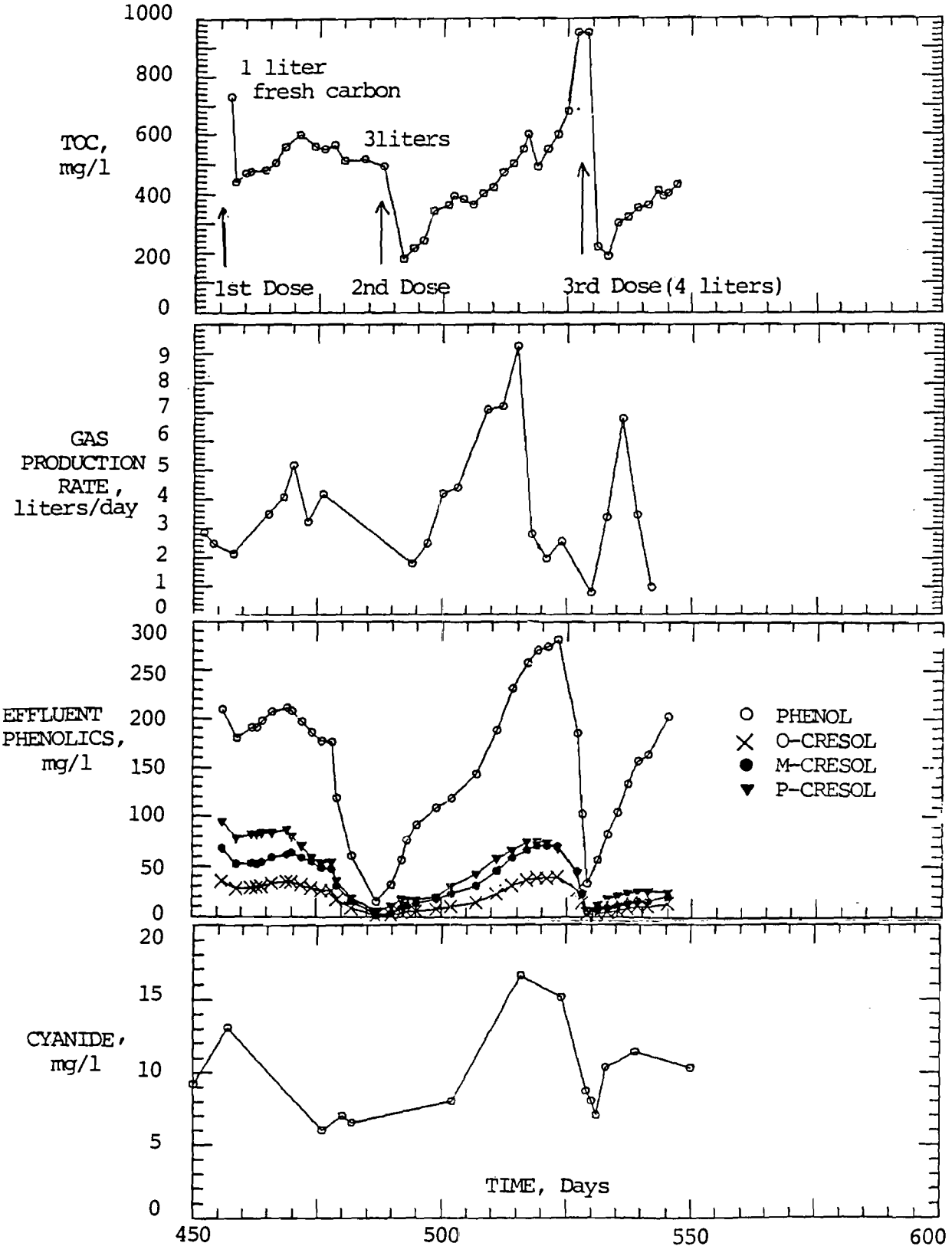

Fig. 13 Performance of System III During Carbon Cycling.

approximately the same volume of gas produced during peak performance of both systems II and III. This fact again seemed to point to the existence of an optimum biological growth condition just beyond initial cresol breakthrough but before total saturation (and the possible breakthrough of other organic and inorganic constituents). Additionally, since phenol breakthrough had previously occurred, its availability as a carbon source for biological growth was at a maximum under this condition. The pragmatic implications of these observations become clear - if the reactor could be operated at biologically conducive conditions for the long term, maximal carbon use and minimum dilution could possibly be realized. The engineering considerations such as reactor design and operational strategies remain to be optimized. Economic feasibility will ultimately depend on these engineering considerations, and the advantages potentially available from efficient use of anaerobic over aerobic stabilization systems.

Moreover, the AFACF provides a degree of treatment beyond that available from activated sludge, since even at long retention times a number of pollutants which are adsorbed in AFACF escape aerobic conversion. Further, the removal of these same pollutants has been observed as being instrumental in determining the efficiency of nitrification and denitrification systems down stream as discussed later.

Series of AFACF Reactors - Carbon Scheduling

From the observed behavior of the AFACF and nitrification process in response to cyclic additions of fresh activated carbon, the necessity of maintaining active adsorption as an *in situ* pretreatment was evident. From an operational viewpoint, carbon replacement should occur as infrequently as possible to avoid downtime and minimize loss of biomass. Two immediate needs arise: a simple and effective method for the physical replacement of carbon, and an operating strategy including a carbon replacement schedule and analytical monitoring procedures.

Insofar as the replacement of carbon is concerned, one approach is a series of reactors representing a moving-bed type of system, wherein reactors are operated until carbon saturation and then temporarily removed from service for carbon bed regeneration and/or replacement. This approach was studied and results are illustrated in Figure 14, which shows that virtually no gas production was observed in the second column in the series (B) until phenol breakthrough occurred. At this point the gas production rate began to slowly increase concomitant with the rise in phenol concentration. The third column in the series did not produce any gas nor have any phenol in the effluent. The first reactor in the series would be removed as soon as the second reactor has attained a stable level of performance. Unfortunately, the second reactor's performance declined before substantial biological activity could be established. Perhaps the microorganisms did not have sufficient time to acclimate to the phenolic carbon sources before the onset of inhibition.

The other carbon replacement strategy studied involved the removal of a percentage of the spent carbon and addition of fresh carbon as previously illustrated in Figure 13. This method also works well, although it requires a greater carbon replacement frequency and more operator time than does the series-reactor approach. Additional plumbing is also required to recirculate process water through carbon addition and removal appurtenances in order to keep the bed anaerobic during replacement operations. This approach allows

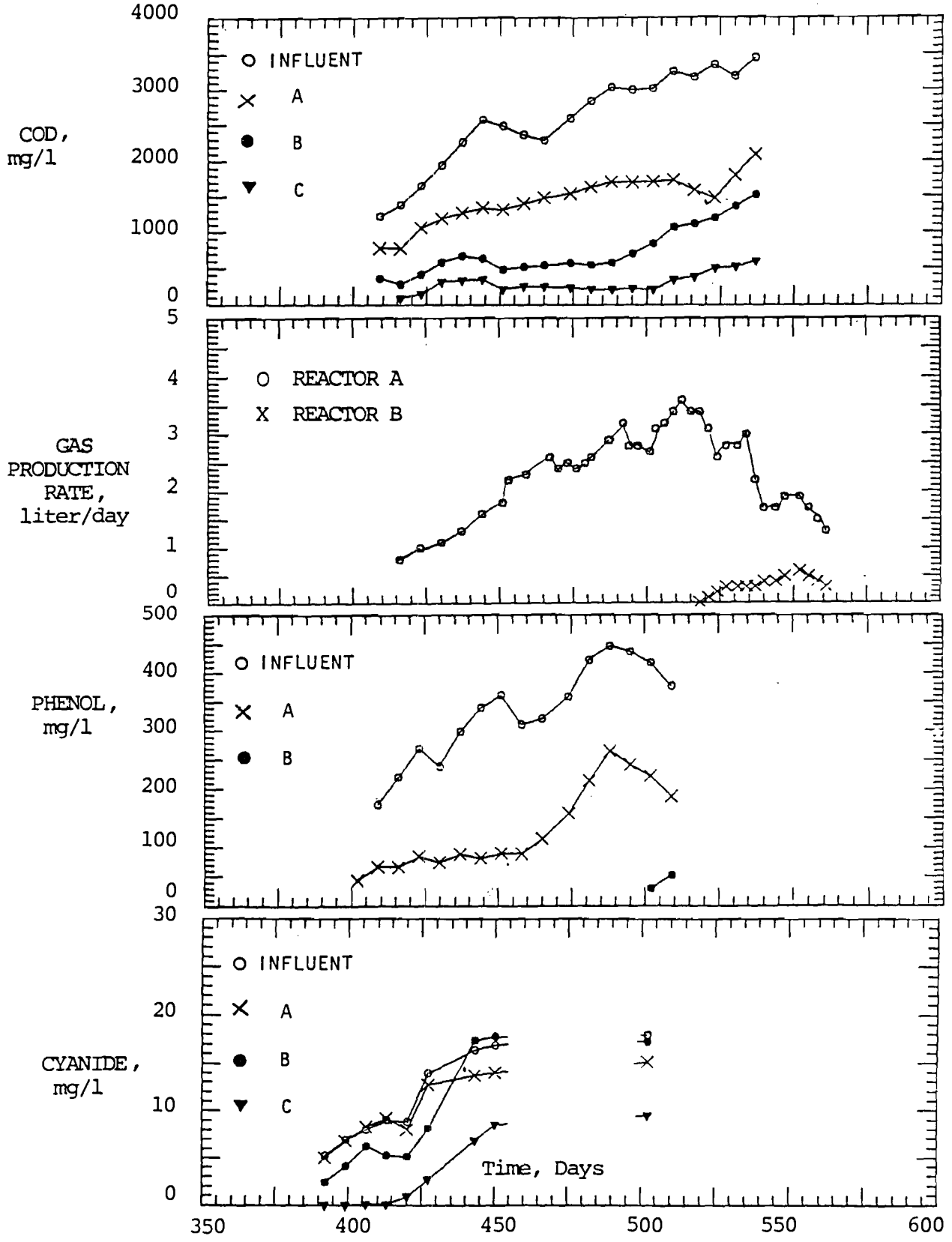

Fig. 14 Performance of Three Carbon Filters In Series - System IV.

for a good deal of flexibility in process control and for rapid generation of operational data from which carbon replacement schedules can be established.

Adsorption Contribution to Wastewater Treatment

The relative contributions of adsorption and biodegradation can be separated through a material balance on carbon as illustrated for system III in Table 7. Table 7 relates the performance of system III for the five months following the last glucose addition. For the period with no glucose in the feed, the table reflects an 80-90% contribution to total carbon (TC) removal by adsorption until biological activity increased around Day 270. During the ensuing two months of peak biological operation (Days 270-340), the adsorption contribution first decreased to 9%, then increased again to 75%, then decreased to zero on Days 334-340 where it appears that bioregeneration (defined as gaseous carbon production in excess of aqueous carbon input) may have occurred.

Biological Contribution to Adsorption

The production of biogas in excess of carbon removal, as witnessed on Days 334 and 340 (Table 7), possibly indicative of bioregeneration, may have served to increase the service life of the activated carbon. A comparison of the breakthrough curve produced for system III to a breakthrough curve generated in the absence of biological activity is shown in Figure 15. The nonbiological breakthrough curve was generated in a 1/2 in. internal diameter I.D. plexiglas column using ten g of 50 x 60 mesh carbon preceded by approximately 5 carbon bed depths of 35 mesh sand. The feed used was effluent which was taken from system III near carbon saturation, then refrigerated and monitored for phenol and cresol stability to assure bioinactivity. Influent phenol and total cresol concentrations were 150 and 190 mg/L, respectively.

The relationship between phenol and cresols for activated carbon (AC) and biological activated carbon (BAC) is illustrated by Figure 15, which shows that total cresol breakthrough for the biological carbon lags behind that of nonbiological carbon by about 200 g of carbon per kg of activated carbon used. This apparent increase in cresol capacity could have been due to bioregeneraton and/or desorption of phenol from the carbon to accommodate cresol adsorption. It can be seen from Figure 15 that phenol desorbed from both nonbiological system (AC) as well as the biological activated carbon (BAC) system. The rate of desorption of phenol appeared to be much greater in the BAC system, thus allowing for the better accommodation of cresols and other higher molecular weight organics. It is interesting to note that the area between the phenol curves for AC and BAC roughly corresponds to the area between cresol curves for AC and BAC in Figure 15.

Suggestion for Operation

The effects of adsorption on the cyanide concentration are also particularly interesting. A decrease in cyanide removal efficiency is observable just following cresol breakthrough during both normal operation and carbon cycling studies. At these times, the cyanide concentration reached nearly 20 mg/L, which may well be a principal cause of inhibition. Similar trends can be seen in the data of Suidan et al. in that on Days 40 to 60 and 140 to 210, the cyanide concentration rose to above 20 mg/L and the process exhibited inhibitory behavior as reflected by decreases in COD and DOC removals[22].

Table 7. Mass Balance on Carbon in System III.

DATE	DAY	INFLUENT TOTAL CARBON, (mg/l)	INFLUENT INORGANIC CARBON, (mg/l)	EFFLUENT TOTAL CARBON, (mg/l)	EFFLUENT INORGANIC CARBON, (mg/l)	TOTAL CARBON REMOVED, (mg/l TC)	GASEOUS CARBON PRODUCED, (mg/l)	DISSOLVED GASEOUS CARBON (mg/l TIC)	ESTIMATED BIOMASS CARBON, (mg/l)*	ADSORBED CARBON, (mg/l)	REMOVED AS ADSORPTION, (%)	REMOVED AS BIOGAS, (%)
5/10	219	1370	160	720	190	650	55	30	10	555	85	13
5/17	226	1320	140	540	120	780	30	20	5	725	93	6
5/24	233	1070	150	660	200	410	60	50	10	290	71	27
5/31	240	1040	220	620	240	420	35	20	5	360	86	13
6/10	250	1040	160	580	160	460	80	0	10	370	80	17
6/16	256	940	140	680	190	260	40	50	10	160	62	35
6/24	264	940	160	670	180	270	35	20	5	210	78	20
7/01	271	970	180	620	180	350	245	0	25	80	23	70
7/08	278	920	180	520	140	450	255	-40	20	215	48	48
7/14	284	960	150	620	220	340	205	70	25	40	12	81
7/21	291	1000	125	660	190	340	215	65	30	30	9	82
7/27	297	1080	140	820	160	260	170	20	20	40	15	73
8/04	305	1060	200	660	190	400	180	-10	15	215	54	42
8/11	312	1090	180	550	180	540	135	0	15	390	72	25
8/18	319	1020	180	420	125	600	190	-55	15	450	75	22
8/25	326	1060	150	680	190	380	240	40	30	70	22	74
9/02	334	1100	190	1020	180	80	200	-10	20	-130	0	100
9/08	340	1140	240	1040	240	100	120	0	10	-30	0	100
9/16	348	1160	200	640	190	520	125	-10	10	385	74	22
9/22	354	1040	120	600	180	400	120	60	20	200	50	45
9/28	360	1060	130	600	170	460	70	40	10	340	74	24

*Estimated as approximately 10% of gaseous carbon produced.

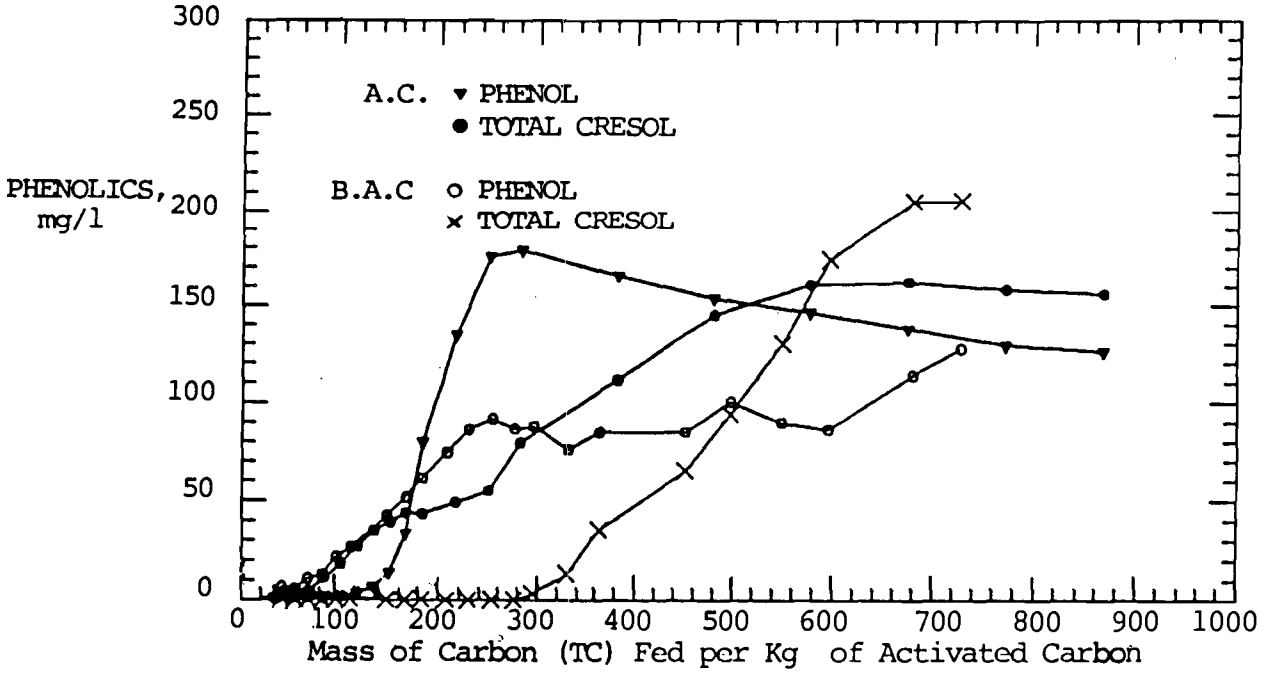

Fig. 15 Comparison of Biological Activated Carbon (BAC) and Non-Biological Activated Carbon (AC) Phenol and Total Cresol Breakthrough Curves

Discernment of the true identity of the inhibitory agent(s) would be of great benefit in optimizing biological process performance; however, it is not entirely necessary for process control. Correlations between process efficiency and monitoring parameters such as cresol, cyanide, gas production, and COD can be used as indicators of carbon saturation and biological activity and therefore serve as key control parameters. Recognition of an accumulation of adsorbable and/or inhibitory constituents in the bulk solution could indicate the need for carbon replacement in advance of biological failure and help maintain optimum operating conditions.

From experiences with 10% dilutions of wastewater, approximately 1.2-1.6 kg of activated carbon were required per kg of carbon fed before total inhibition occurred. At loading rates of 15 g of carbon/day this corresponded to around 50 days of operation per kg of activated carbon. Carbon cycling studies indicated a slightly higher frequency of carbon replacement is necessary to assure a high biological conversion rate; around 25 days of operation per kg of activated carbon seem optimum.

For carbon cycling operations, removal of around 25% of the bed volume does not seem to severely affect conversion; however, removal of a larger amount may necessitate a reacclimation period due to excessive biomass removal. For the series reactor approach, reactor size will ultimately be determined by the safety level desired in terms of biological activity overlap between sequential reactors and the degree of effluent polishing desired by adsorption.

Carbon cycling studies and series-reactor data have been combined with initial operational data on three separate reactor systems to suggest carbon replacement frequencies necessary for optimum biological-adsorptive process performances. A carbon replacement frequency of approximately 0.6-0.8 kg AC per kg of carbon fed (25 days/kg AC) seems biologically optimal. For a removal/replacement approach, no more than 25% of the bed volume should be removed at a time in order to avoid excessive loss of biomass.

NITRIFICATION STUDY

The nitrification experiments lasted 367 days and were divided into five phases - acclimation phase, pseudo-steady state operation, inhibition, period of powdered activated carbon addition to the aeration basin, and period of granular activated carbon replacement in the anaerobic filter for removal of compounds inhibitory to nitrification (Table 8). Note that from Days 132 through 160, the nitrification system was short of feed several times; therefore samples were not routinely obtained and not data were reported.

Acclimation Phase. During Phase 1 of the study (Days 1 to 56), a nitrifying activated sludge obtained from a local pure oxygen wastewater treatment plant (South Cobb Plant, Austell, GA) was gradually acclimated to the anaerobic filter effluent which contained approximately 600 mg TKN/L (527 mg NH_3-N/L). In the acclimation procedure (Table 9), the feed concentration (of the anaerobic filter effluent to the nitrification system) was increased in five steps from 10% to 100% anaerobic effluent. Each step increase in feed concentration during the acclimation phase lasted from 8 to 13 days.

Throughout the acclimation phase, the hydraulic retention time (HRT) was maintained at 18 hours and the solids retention time (SRT) was maintained at 22 days beginning with Period 1c (Table 9). Loadings were gradually increased from 0.06 to 0.23 kg NH_3-N/kg MLVSS·day and from 0.09 to 0.43 kg COD/kg MLVSS·day by increasing the concentration of anaerobic effluent fed to the system. Figure 16a (Days 1 to 56) indicates that effluent NH_3-N level occasionally increased suddenly at the beginning of each step but after 2 to 3 days, it decreased rapidly to its original level again. However, in other cases, there were no changes in final effluent ammonia from one step to another, indicating that the activated sludge could quickly acclimate to the feed change.

Table 9 also shows that during the acclimation phase as much as 99% of the NH_3-N was removed; effluent NH_3-N was less than 2 mg/L and almost all NH_3-N was converted to NO_3^--N. During the acclimation phase, COD and TOC removal increased from 40% initially to 80% at the end of the test period. Aeration basin MLSS increased from 1563 mg/L to 3167 mg/L during this same period.

Pseudo-Steady-State Operation. After acclimation, pseudo-steady-state operation of the nitrification system was attained. The system was first operated at the HRT and SRT used in the acclimation phase, (18 hours and 22 days, respectively). Data obtained during Period 2a (Days 57 to 82) showed that, although effluent COD and TOC were relatively constant (206 mg/L and 127 mg/L, respectively, Figure 16b), effluent NH_3-N gradually increased from 2 mg/L to 46 mg/L (Figure 16a) and effluent NO_2^--N increased as well (Figure 16c, Days 48 to 76). This indicated some inhibition of the nitrification process under these operating conditions. The SRT was increased from 22 to 31 days and the HRT from 18 to 30 hours; correspondingly, NH_3-N loading decreased from 0.27 to 0.15 kg NH_3-N/kg MLVSS·day and COD loading from 0.52 to 0.35 kg COD/kg MLVSS·day. Figures 16a and 16b (Period 2b, Days 83 to 132), indicate that, under these new operating conditions, the effluent quality from the nitrification system was very stable although influent COD and TOC continuously increased. However, a peak of approximately 125 mg NO_2^--N/L occurred in the last several days of Period 2b (Figure 16c, Days 123 to 132).

Table 8. Phases of Nitrification Experiments.

PHASES OF NITRIFICATION EXPERIMENTS

Phase 1	Acclimation	Day	0 - 56
Phase 2	Pseudo-steady state operation		57 - 132
Phase 3	Inhibition		160 - 203
Phase 4	Addition of PAC to aeration tank		204 - 249
Phase 5	Replacement of GAC in anaerobic filter		250 - 367

No data available during day 133 - 159

Table 9 Operating conditions and performance of nitrification system

Phase	Duration (days)	Period	Time (day)	Duration (days)	Dilution Ratio	SRT (days)	HRT (hrs)	NH_3-N loading	COD loading
1	56	1-a	1-13	13	1:9		18	0.06	0.09
		1-b	14-23	10	1:3		18	0.09	0.14
		1-c	24-31	8	1:1	22	18	0.15	0.14
		1-d	32-44	13	1:0.33	22	18	0.18	0.28
		1-e	45-56	12	1:0	22	18	0.23	0.43
2	76	2-a	57-82	26	1:0	22	18	0.27	0.52
		2-b	83-132	50	1:0	31	30	0.15	0.35
3	44		160-203	44	1:0	26→40	25→33	0.17→0.13	0.43→0.33
4	46	4-a	204-218	15	1:0	31	30	0.20	0.61
		4-b	219-249	31	1:1	31	43	0.08	0.24
5	118	5-a	250-277	28	1:1	30	30	0.08	0.20
		5-b(1)	278-303	26	1:0	30	18	0.18	0.24
		5-b(2)	304-325	22	1:0	30	30	0.15	0.40
		5-c	326-367	42	1:0	30	30	0.15	0.36

Phase: 1. Acclimation; 2. Pseudo-steady state operation; 3. Inhibition; 4. Addition Of powdered activated carbon to aeration basin; 5. Periodical replacement of granular activated carbon in anaerobic filter.

Dilution ratio: Ratio of parts of anaerobic effluent to parts of tap water.

Unit of NH_3-N loading: kgNH_3-N/kgMLVSS/day.

Unit of COD loading: kgCOD/kgMLVSS/day.

Period	TOC(mg/l) Inf	Eff	Rem%	COD(mg/l) Inf	Eff	Rem%	NH_3-N(mg/l) Inf	Eff	Eff NO_2^--N mg/l	Eff NO_3^--N mg/l	MLSS mg/l	Alkalinity consumption
1-a	48	28	42	99	60	39	65	0.8		56	1563	5.6
1-b	110	30	73	182	48	74	111	0.4	0.3	101	1902	5.7
1-c	227	46	80	256	91	64	263	1.8	2.4	221	2655	6.0
1-d	466	56	88	613	91	85	397	1.6	0.3	369	3294	6.1
1-e	692	131	81	895	196	78	485	2.1	10	419	3167	5.6
2-a	594	125	79	894	210	77	473	23	64	341	2509	5.5
2-b	776	72	91	1286	189	85	527 (TKN601)	4.4 (TKN18.3)	16	485	3238	5.8
3				1364	455	67	543	30→520	85	466→18	3318	
4-a				1711	398	77	558	414	24	16	2715	
4-b				955	204	79	294	208→1.8	12	25→295	2451	
5-a				682	84	88	260	1.9	0.3	194	2911	5.9
5-b(1)				680	92	86	515	3.7	0.5	476	4188	6.7
5-b(2)				1810	369	80	682	142→3.0	384→0.7	346→700	4153	
5-c				1393	184	87	579	7.0	4.2	597	3411	7.2

Unit of alkalinity consumption: mg Alkalinity consumed/mg NH_3-N removed

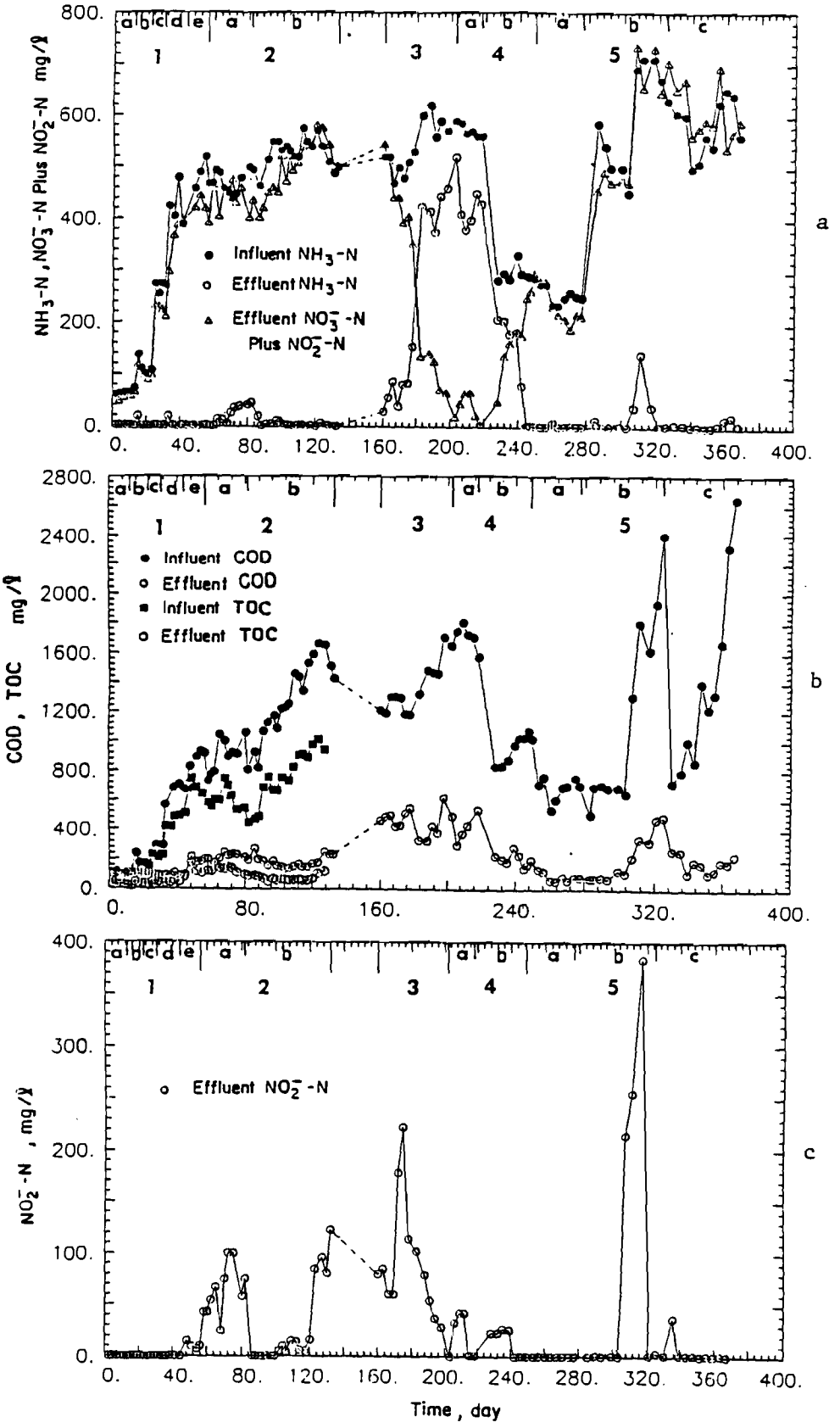

Fig. 16 Nitrification System NH_3-N, NO_3^--N, NO_2^--N, COD, TOC Concentrations

Based on the data in parentheses in Table 9, TKN removal during this period was as high as 97% with effluent TKN of 18 mg/L. The effluent NH_3-N was only 4.4 mg/L, whereas effluent NO_3^--N was 485 mg/L. The corresponding COD and TOC removals were 95% and 91%, respectively. These data indicated that nitrification was relatively complete and organic matter reduction was high.

As shown in Table 10, a nitrogen balance was performed for a 30-day span during Period 2b (Days 97 to 127). The average effluent TKN, NO_3^--N and NO_2^--N accounted for 3%, 83.7% and 3.5% of the influent TKN, respectively. The total effluent nitrogen was 90.2% of the influent TKN or only 9.8% of the influent TKN was unaccounted for (the percentage of unaccounted nitrogen varying from 1.0% to 18.1%). This unaccounted portion of influent TKN was attributed to microbial cell growth and possible denitrification, air stripping, and analytical error.

The production of sludge was estimated during the same period. On the average, the sludge growth rate was 1.2 g/day and COD removed was 9.5 g/day. The computed yield coefficient was 0.13 kg sludge formed/kg COD removed, which was consistent with data obtained by Olthof[25] for coke oven wastewater treatment. Calculated alkalinity consumption for the same period was 5.8 mg alkalinity consumed/mg NH_3-N removed.

Inhibition of Nitrification. The anaerobic filter effluent quality began to deteriorate from saturation of the activated carbon in the filter with refractory compounds such as cresols after 10 months of operation. The effluent COD eventually increased to 2100 mg/L with only 30% COD removal. Correspondingly, effluent phenol from the anaerobic filter increased to 270 mg/L with only 50% phenol removal and effluent total cresols increased to 230 mg/L without any evidence of cresol removal. That the poorer quality of anaerobic effluent resulted in inhibition of the nitrification process can be seen from Figure 16a where from Day 160 the performance of the nitrification system began to deteriorate. By Day 203 the system was almost completely inhibited and effluent NH_3-N was as high as 520 mg/L and effluent NO_3^--N plus NO_2^--N as low as 18 mg/L. Although the SRT and HRT were increased to 40 days and 33 hours, respectively, and an automatic pH controller was installed in the aeration basin to maintain pH between 7.0 and 7.5, the system performance did not improve.

As shown in Table 9, the loadings to the nitrification system during the inhibition period (Phase 3) were maintained at 0.17 to 0.13 kg NH_3-N/kg MLVSS·day and 0.43 to 0.33 kg MLVSS·day, comparable to those during pseudo-steady-state operation (Phase 2). Other operating parameters such as pH, alkalinity, and DO were also normal. The inhibition of the nitrification system might, therefore, have been attributable to the presence of some inhibitory compounds in the influent of the nitrification system; the most likely candidates were CN^-, SCN^-, S^{-2}, phenol, cresols, and other trace organic compounds in the coal gasification wastewater. However, analytical determinations indicated that the influent concentrations of CN^-, SCN^- and S^{-2} in the nitrification system were within the range of 3 to 17 mg/L, 4 to 20 mg/L, and 2 to 5 mg/L, respectively. Results reported in the literature[4-6, 22, 24-27] indicate no inhibition to nitrifying organisms attributable to these compounds at these concentrations.

Table 10. Nitrogen Balance Data (Day 97-127)

Day	Inf.	Eff.				Total N not accounted for	
	ΣN_{inf}=TKN	TKN	NO_2^--N	NO_3^--N	ΣN_{eff}*	$\Sigma N_{inf}-\Sigma N_{eff}$	%
97	580	24.5	0.7	450	475	105	18.1
99	555	20.9	0.4	520	541	14	2.5
102	580	15.0	5.0	468	488	92	15.9
104	595	15.5	10.2	512	538	57	9.6
106	590	14.0	3.9	490	508	82	13.9
109	595	14.2	14.7	494	523	72	12.1
112	625	19.5	14.1	524	557	68	10.9
114	615	16.2	5.9	536	558	57	9.3
117	635	15.8	4.6	536	556	79	12.4
120	635	13.6	16.0	564	594	41	6.5
123	635	23.5	85.0	490	598	37	5.8
127	575	27.2	96.0	446	569	6	1.0
Ave.	601	18.3	21.4	503	542	59	9.8
% of Inf TKN	100	3.0	3.5	83.7	90.2	9.8	

All values are in mg/L except for percentages.

*ΣN_{eff}=TKN + NO_2^--N + NO_3^--N

Similarly, phenol in the influent to the nitrification system varied from 53 mg/L to 409 mg/L, and in most cases could be removed completely in the system as shown in Figure 17a. As indicated by several investigators[4,24,26] phenol concentrations much higher than 400 mg/L could be removed entirely in the activated sludge process. Therefore, the inhibition of the nitrification system was not attributed to the presence of phenol.

Tomlinson, et al.[28] reported that nitrification (using activated sludge as a source of nitrifying bacteria) was inhibited by 12.8 mg/L o-cresol, 11.4 mg/L m-cresol, and 16.5 mg/L p-cresol. Suidan et al.[22] showed that 7.8 mg/L o-cresol and 12.1 mg/L m-cresol and p-cresol could be removed completely without causing any inhibition. This may have been the result of a difference in the acclimated activated sludge. In this study, in all cases influent o-cresol concentrations from 3 to 46 mg/L were readily removed in the nitrification system (Figure 17b). However, only 80% of m-cresol and p-cresol was removed during the inhibition phase (Days 160 to 218); 20 to 35 mg/L remained in the effluent (Figure 17c). This level of m-cresol and p-cresol concentrations were implicated as a cause of nitrification inhibition although they could not be specifically identified as the sole inhibiting compounds. Because of the complex composition of the coal gasification wastewater, results shown in Figure 16a and Figure 16c (Days 244 to 304, and 321 to 367) indicated that when the total concentration of m-cresol and p-cresol in the nitrification effluent was less than 5 mg/L, the system performed very well with complete NH_3-N removal. However, when the effluent concentrations were higher than 15 mg/L (Figure 17c, Days 160 to 220 and 311), the system showed signs of inhibition (Figure 16a) with corresponding increases in effluent NH_3-N.

In general, there are two types of microorganisms that exist simultaneously in the activated sludge of a single-stage nitrification process. One is the autotrophic nitrifiers that convert NH_3-N to NO_2-N and NO_3^--N and are extremely sensitive to inhibitory compounds. The other is the heterotrophic microorganisms responsible for removal of organic compounds. In this study, the ratios of COD to NH_3-N normally ranged from two to four and the heterotrophs accounted for a substantial fraction of microorganisms in the activated sludge[29]. Therefore, phenol and o-cresol in all cases, and m-cresol and p-cresol in most cases could be completely removed by the heterotrophs; effluent concentrations were below detection limits. The autotrophs were not inhibited and complete nitrification occurred. However, if influent m-cresol and p-cresol were more than, for example, 150 mg/L, although 80% of m-cresol and p-cresol could be removed by the heterotrophs, the remaining 30 mg/L of m-cresol and p-cresol in the aeration basin could inhibit the autotrophs and lead to nitrification inhibition.

Recovery of Nitrification from Inhibition. Addition of powdered activated carbon (PAC) improves the performance of nitrification by partial or complete removal of inhibitory compounds[30-33]. PAC was added to the nitrification system to restore the system to its original operating efficiency. During Phase 4 of the study, the initial carbon equilibrium concentration was 2500 mg/L in the aeration basin. A daily dose of PAC was added to supplement the loss of PAC from withdrawal of PAC-activated sludge mixed liquor to maintain the SRT. The dose corresponded to 100 mg/L of PAC added to the influent of the nitrification system. At a 31-day SRT and a 30-hour HRT, there was no apparent improvement in the nitrification system.

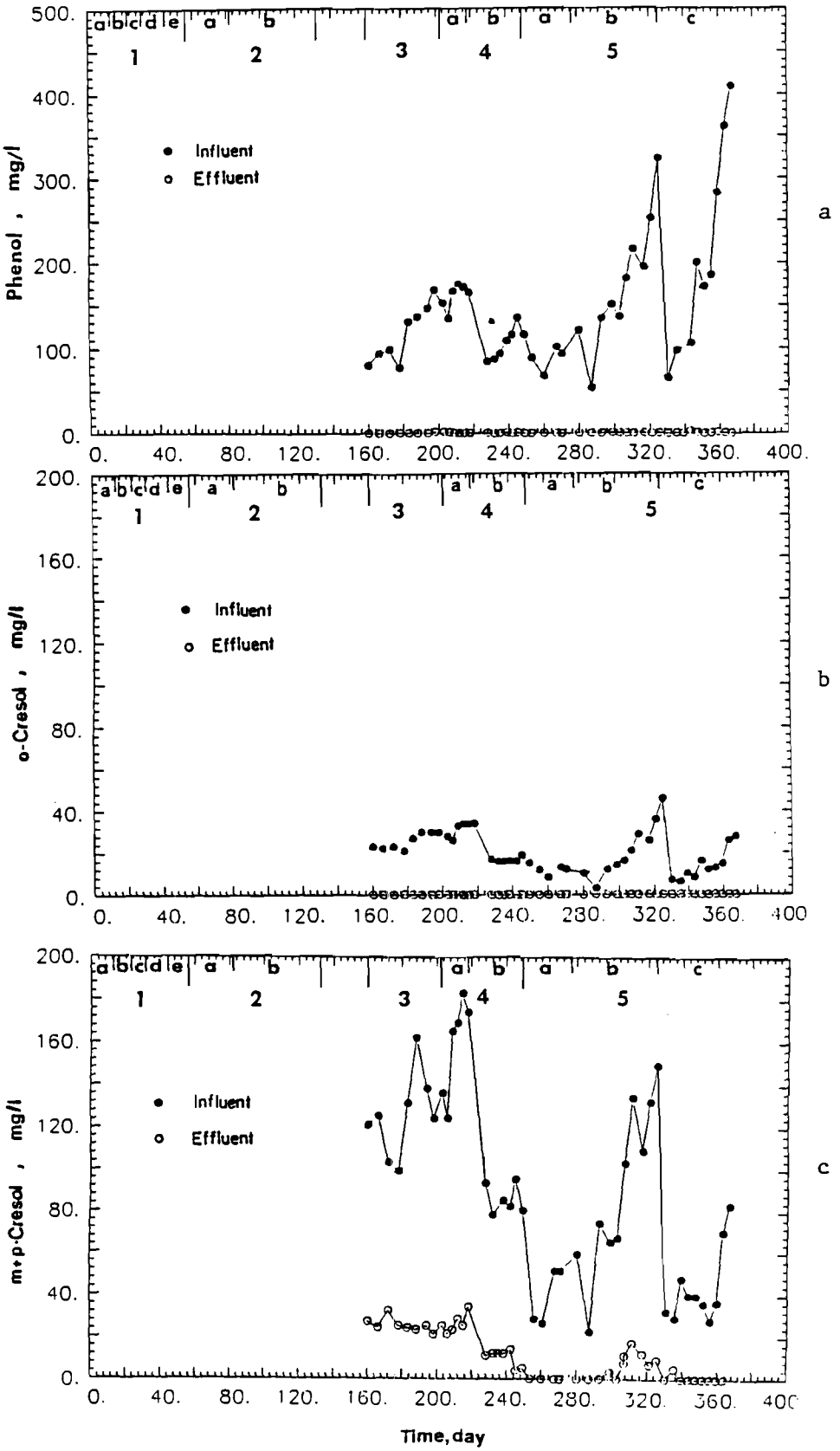

Fig. 17 Nitrification System Phenol, Cresol Concentrations

Average effluent NH_3-N was 414 mg/L, and NO_3^--N plus NO_2^--N totalled 40 mg/L (Figure 16a, Period 4a, Days 204 to 218). The PAC concentration, with respect to the influent was, therefore, increased to 150 mg/L by decreasing the influent flow rate to two-thirds of its original value. At the same time, the influent was diluted one-to-one with tap water to expedite the recovery of the system from inhibition. As shown in Figure 16a and Figure 16c (Period 4b, Days 129 to 249) under the new SRT of 31 days and HRT of 43 hours, the nitrification system recovered very rapidly. NH_3-N in the effluent decreased from 208 mg/L to 3 mg/L, effluent NO_3^--N increased to 250 mg/L (Figure 16a), and effluent NO_2^--N decreased to 0.3 mg/L (Figure 16c).

In the meantime, a portion of the granular activated carbon (GAC) was periodically replaced to improve the performance of the anaerobic filter beginning on Day 250. At that time, PAC addition was discontinued. The system was operated at a one-to-one dilution until Day 278, at which time the system began receiving undiluted anaerobic filter effluent. As can be seen from Figure 16b, 17a, 17b and 17c (Phase 5, Days 250 to 367), each time a portion of the GAC in the anaerobic filter was replaced (Days 250, 278, and 326), the anaerobic effluent quality improved significantly. For instance, COD, phenol, and cresols were reduced markedly, but over time their concentrations increased rapidly again. Although influent NH_3-N was relatively stable throughout each carbon replacement in the anaerobic filter, influent COD, phenol, and cresol varied significantly from the beginning to the end of each replacement period. However, the salient feature appeared during Phase 5 when the influent m-cresol and p-cresol in the nitrification system were much lower than during inhibition Phase 3a (except for Days 307 to 321 during which period a sudden increase in feed concentrations caused temporary nitrification inhibition, when effluent NH_3-N increased and effluent m-cresol and p-cresol concentrations exceeded 15 mg/L). Therefore, during Phase 5 the nitrification system performed well and the effluent NH_3-N remained very low (Figure 16a, Days 250 to 367).

Table 9 shows that during Periods $5b^1$, $5b^2$, and 5c (except Days 307 to 321) with undiluted anaerobic effluent used as feed, the nitrification system was operated at an SRT of 30 days, NH_3-N loading of 0.15 to 0.18 kg NH_3-N/kg MLVSS·day, and COD loading of 0.24 to 0.40 kg COD/kg MLVSS·day, similar to the operating conditions during the pseudo-steady-state operation Period 2b. System performance was excellent during Periods 5b and 5c; NH_3-N removal (99%) and COD removal (86%) matched those obtained in Period 2b.

A second nitrification system with the same configuration as the first, and seeded with activated sludge from the first nitrification system obtained during the inhibition period, was started and received effluent from a new anaerobic activated carbon filter system on Day 206. Because most of the organic compounds, including cresols, were removed by the newly installed anaerobic filter, the second nitrification system recovered completely in only 12 days and was continuously operated for 150 days with no sign of inhibition caused by organic compounds as shown in Figure 18. From Figure 18 it can also be seen that there were several peaks in effluent NH_3-N concentration, in most cases resulting from pH less than 6.5, and in the last case also from low DO (0.4 mg/L). After adjustment of pH and DO in the aeration basin, the effluent NH_3-N was reduced rapidly to its original concentration of less than 5 mg/L.

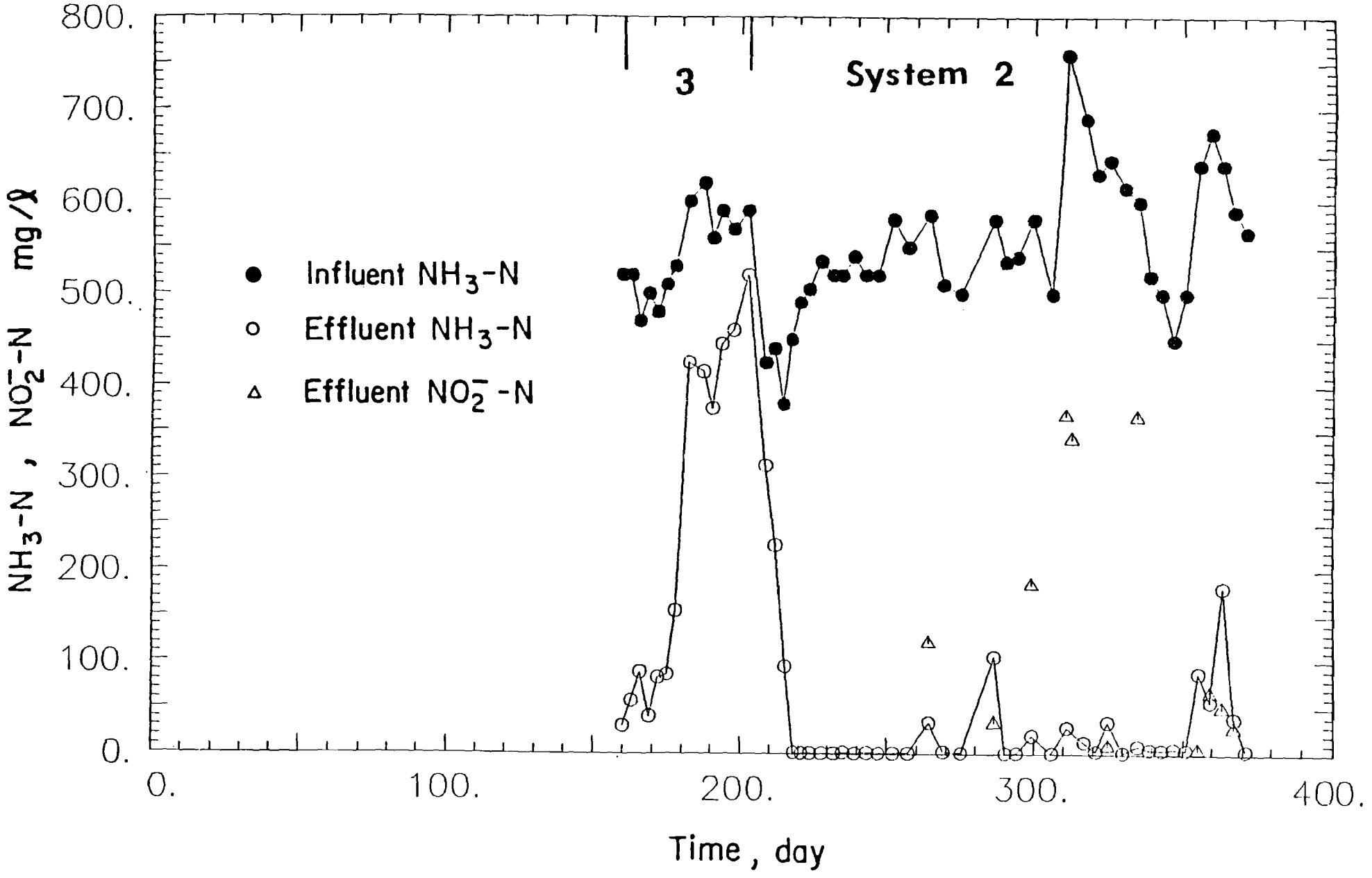

Fig. 18 Ammonia Removal and NO_2^--N Accumulation in the Second Nitrification System

Solids Retention Time. As is well known, the nitrification process is characterized by the fact that the growth of autotrophic nitrifying organisms is very much slower than that of heterotrophs and the reaction rate of nitrification is correspondingly slower. This means that to maintain a population of nitrifiers, the SRT must be long enough to avoid "wash out" of nitrifying organisms from the system. The published research on nitrification of wastewater containing high concentrations of ammonia, was conducted with an SRT of 20 days or more and an NH_3-N loading of 0.01 to 0.5 kg NH_3-N/kg MLVSS·day. In this study the SRT was 22 days and 31 days and the NH_3-N loading was 0.27 and 0.15 kg NH_3-N/kg MLVSS·day. This is consistent with the data cited above. In general, the performance of the nitrification system seemed to become better and more stable under the conditions of longer SRT and lower NH_3-N loading.

NO_2^--N Accumulation. Incomplete nitrification occurred in some studies[27,30,33,34] and ammonia was mainly oxidized to nitrite rather than nitrate, which lead to NO_2^--N accumulations. In this study NO_2^--N accumulation occurred in certain cases. Figures 16a, and 16c indicate that NO_2^--N gradually increased during Period 2b (Days 83 to 132) without an increase in effluent NH_3-N. Otherwise, NO_2^--N accumulation always occurred with an increase of effluent NH_3-N during partial inhibition of nitrification (Days 57 to 82, 160 to 184, 307 to 321). Furthermore, pH control is a very important operating parameter for nitrification of high strength ammonia wastewaters. The aeration basin pH sometimes dropped to less than 6.5 because of insufficient supplementary alkalinity in the feed and resulted in temporary increases in effluent NO_2^--N as shown in Figure 18. However, as long as the pH in the aeration basin was adjusted to between 7 and 8, the effluent NO_2^--N disappeared immediately.

Sludge Settling Characteristics. A problem encountered in some nitrification studies was that the MLSS maintained in the aeration basin was too low and effluent suspended solids were too high as a result of poor settling in the clarifier. Filamentous organisms grew at high loadings in the absence of trace nutrients[26,34]. In the present study, the activated sludge had good settling characteristics; the SVI was around 100 (from 34 to 195) and no filamentous organisms were observed by microscopic examination. The MLSS in the aeration basin were maintained at 3000 mg/L (from 1563 to 4188). However, occasional sludge accumulations in the bottom of the clarifier because of problems with the sludge scraper and sludge recycle apparatus, resulted in denitrification and production of a large block of floating sludge which, in turn, temporarily led to high suspended solids in the effluent.

CONCLUSIONS

From the results of these investigations the following conclusions can be drawn:

- A single-stage activated sludge nitrification system was successfully used for removal of ammonia-nitrogen from the effluent of an anaerobic filter treating 10% coal gasification wastewater containing as much as 601 mg TKN/L.

- Performance of the nitrification system was significantly dependent on the effluent quality of the anaerobic fluidized-bed activated carbon filter.

Under the normal 32-day SRT and loadings of 0.15 kg NH_3-N MLVSS·day and 0.35 kg COD/kg MLVSS·day, removals of 97% TKN, 91% TOC and 95% COD were achieved.

- For effective nitrification of the coal gasification wastewater, solids retention time should be more than 22 days.

- Residual phenol and o-cresol could be completely removed in the nitrification system in all cases, but m-cresol and p-cresol removal depended on their influent concentrations. In some instances, the total amount of effluent m-cresol and p-cresol exceeded 15 mg/L and inhibition of the nitrification process occurred.

- Addition of powdered activated carbon to the nitrification system or periodic replacement of a portion of granular activated carbon in the anaerobic filter removed or reduced the concentration of the inhibitory compounds and eliminated inhibition of nitrification.

- Nitrogen balances indicated that the total effluent nitrogen accounted for 90.2% of influent TKN; the unaccounted nitrogen was attributed to microbial cell growth requirements and possible losses from denitrification, air stripping, and analytic error.

- Alkalinity consumption averaged 5.8 mg alkalinity consumed/mg NH_3-N removed.

DENITRIFICATION STUDY

A 283-day study was conducted to study the denitrification of anaerobically treated and nitrified coal gasification effluent. The study was divided into three phases: 1 - acclimation; 2 - stable operation with a relatively constant mean cell residence time (MCRT) using methanol as an external carbon source; and 3 - stable operation with a relatively constant MCRT substituting phenol for methanol as the carbon source. During phase 2 of the operation, two-substrate limitations were imposed on the system. The first was nitrate limitation, where nitrate was not sufficiently available to bacteria for the oxidation of methanol. The second was methanol limitation, where methanol was not available in sufficient quantity to bacteria to reduce all of the nitrate-nitrogen in the influent. The summary of these phases are presented in Table 11.

Phase 1

During the first 99 days microorganisms were acclimating to a new environment. The concentration and total mass of suspended solids in the reactor during this period are presented in Figures 19 and 20. To accelerate this phase, i.e., acclimation, for a period of 19 days, some of the solids in the effluent were settled by gravity and returned manually to the reactor. The initial mass of suspended solids in the reactor was 5 g and concentration of suspended solids was 0.5 g/L, which remained relatively constant until Day 560, as presented in Figures 19 and 20. During this period, Day 541 to 560, the concentration of nitrate-nitrogen in the effluent decreased from 420 mg/L to 100 mg/L (see Figure 21), indicating that the microorganisms responsible for denitrification were acclimating and accumulating in the system. The TOC concentration in the influent ranged between 350 and 950 mg/L, and the TOC concentration in the effluent varied between 100 and 550 mg/L from Day 541 to 560 (see Figure 22). The large variation in TOC concentration in the influent is due to the unmixed solution of methanol, which is discussed in more detail later. The variation in TOC of the effluent was due to the influent TOC.

From Day 561 to 637, the concentration of solids increased from 0.5 g/L to 5.5 g/L (see Figure 19), and as a result, all the nitrate-nitrogen in the effluent disappeared, indicating that denitrifying microorganisms had accumulated to a sufficient level. The TOC concentration in the influent varied between 50 and 2300 mg/L and in the effluent ranged between 50 and 1250 mg/L during this period (these variations are due to the same reason mentioned above). In addition, the contribution of TOC from the coal gasification wastewater is illustrated in Figure 22. As illustrated in Figure 22, the TOC concentration of coal gasification wastewater is much lower than the difference between the influent and effluent TOC concentration. This is the main reason that methanol, as an external carbon source, was used.

Phase 2

Phase 2 of the study began on Day 641 and continued for 134 days. During this phase, two-substrate limitations, nitrate-nitrogen and methanol, were imposed to study the performance of the denitrification under these conditions. From Day 641 to 775, a predetermined amount of solids were wasted from the reactor (see Figure 23). Due to this wastage, the concentration of suspended solids was maintained at a relatively constant level (see Figure 19). The total mass of solids lost during daily operation, as a result of solids lost in the effluent as well as those wasted directly from reactor, is presented in

Table 11. Summary of Denitrification Operational Phases

Phases	Type of Operation	Carbon Source	Period* (day)	Duration (day)
1	Acclimation	Methanol	541-640	99
2	Stable operation with a relatively constant MCRT	Methanol	641-774	134
3	Stable operation with a relatively constant MCRT	Methanol	776-825	50

*Indicated period is consistent with day designation used on anaerobic filter portion of project, i.e., anaerobic filter operation was started on Day 1.

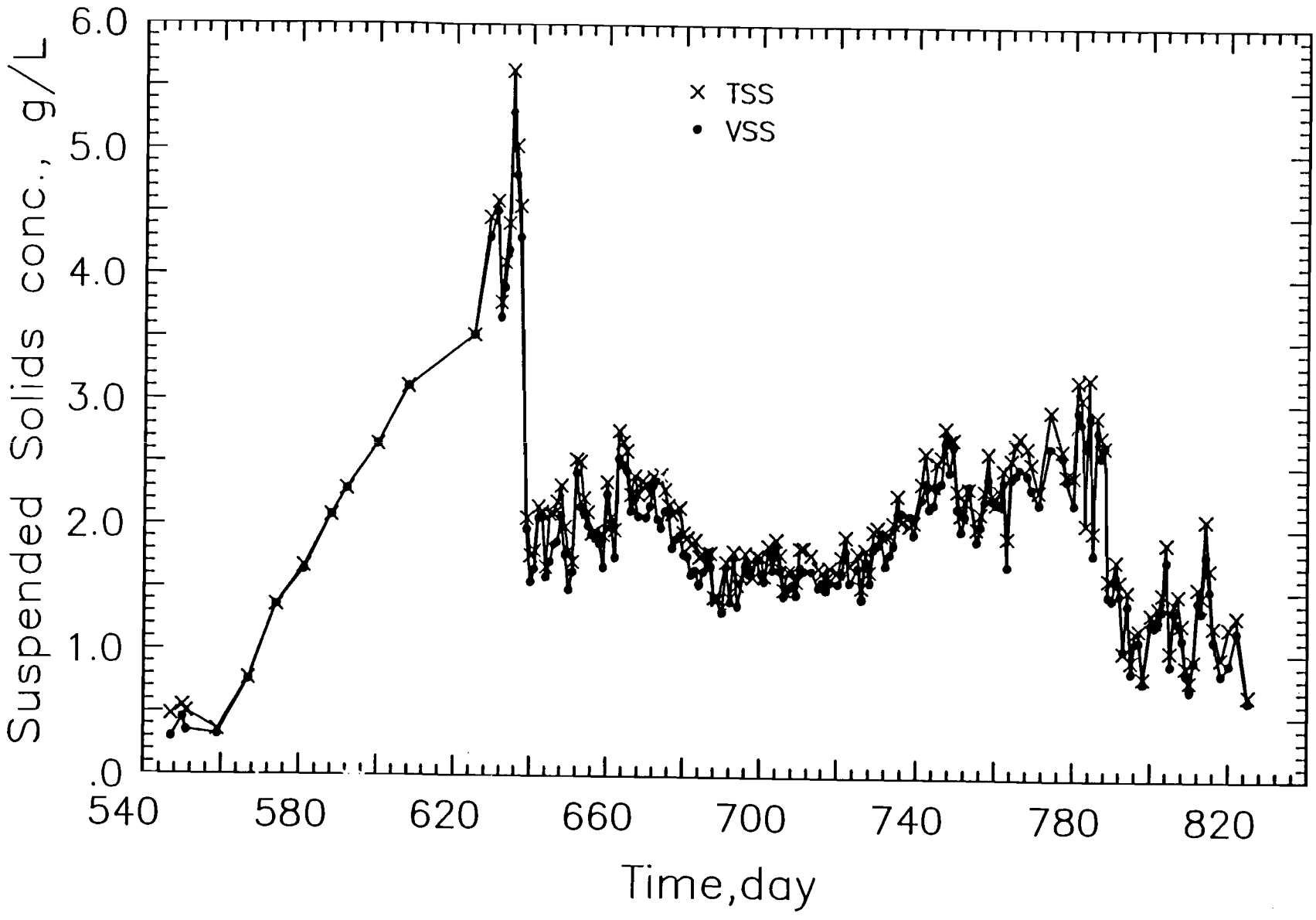

Fig. 19 Suspended Solids, Denitrification Reactor.

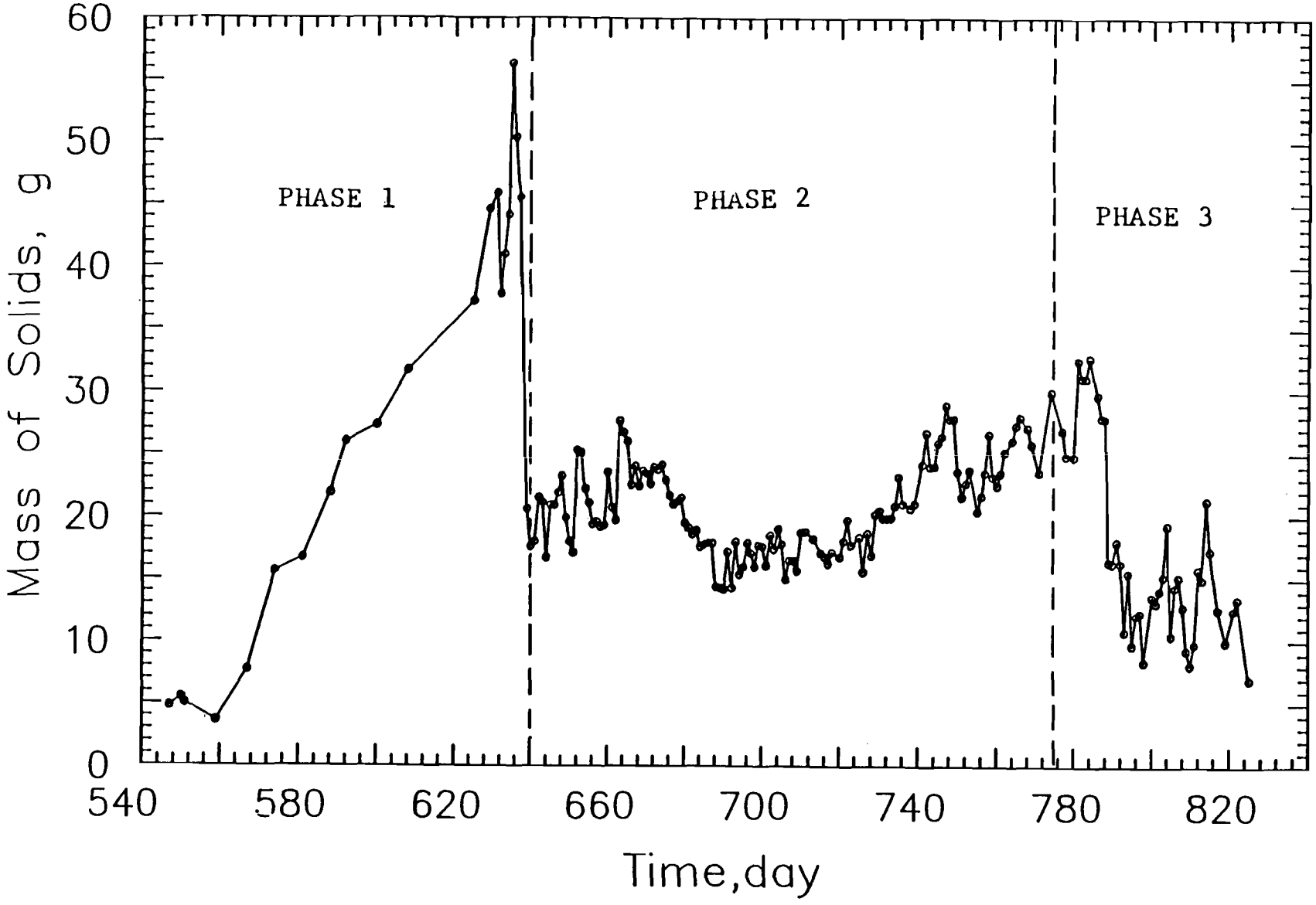

Fig. 20 Total Solids, Denitrification Reactor.

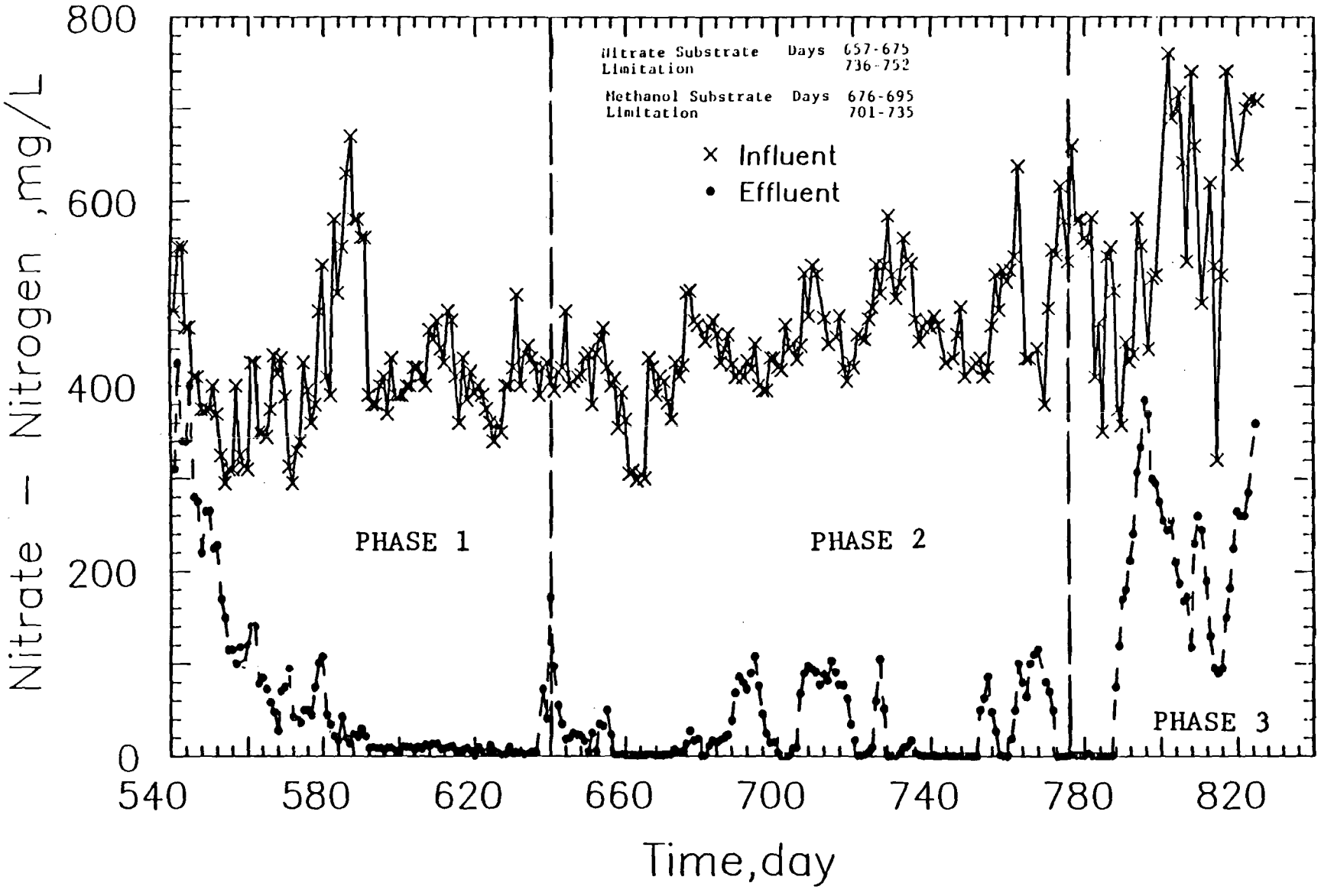

Fig. 21 Nitrate Concentration, Denitrification Reactor.

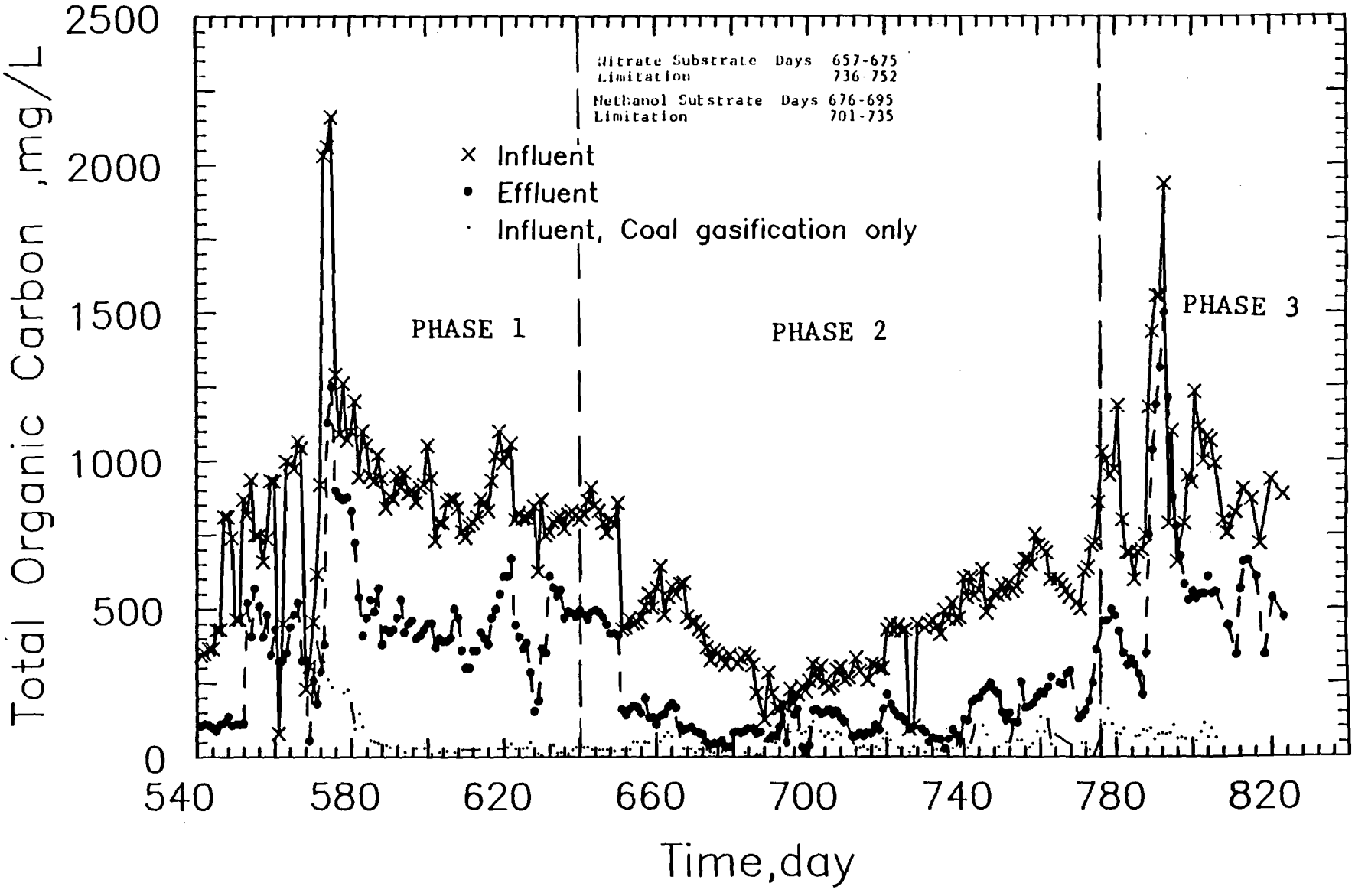

Fig. 22 Total Organic Carbon Concentration, Denitrification Reactor.

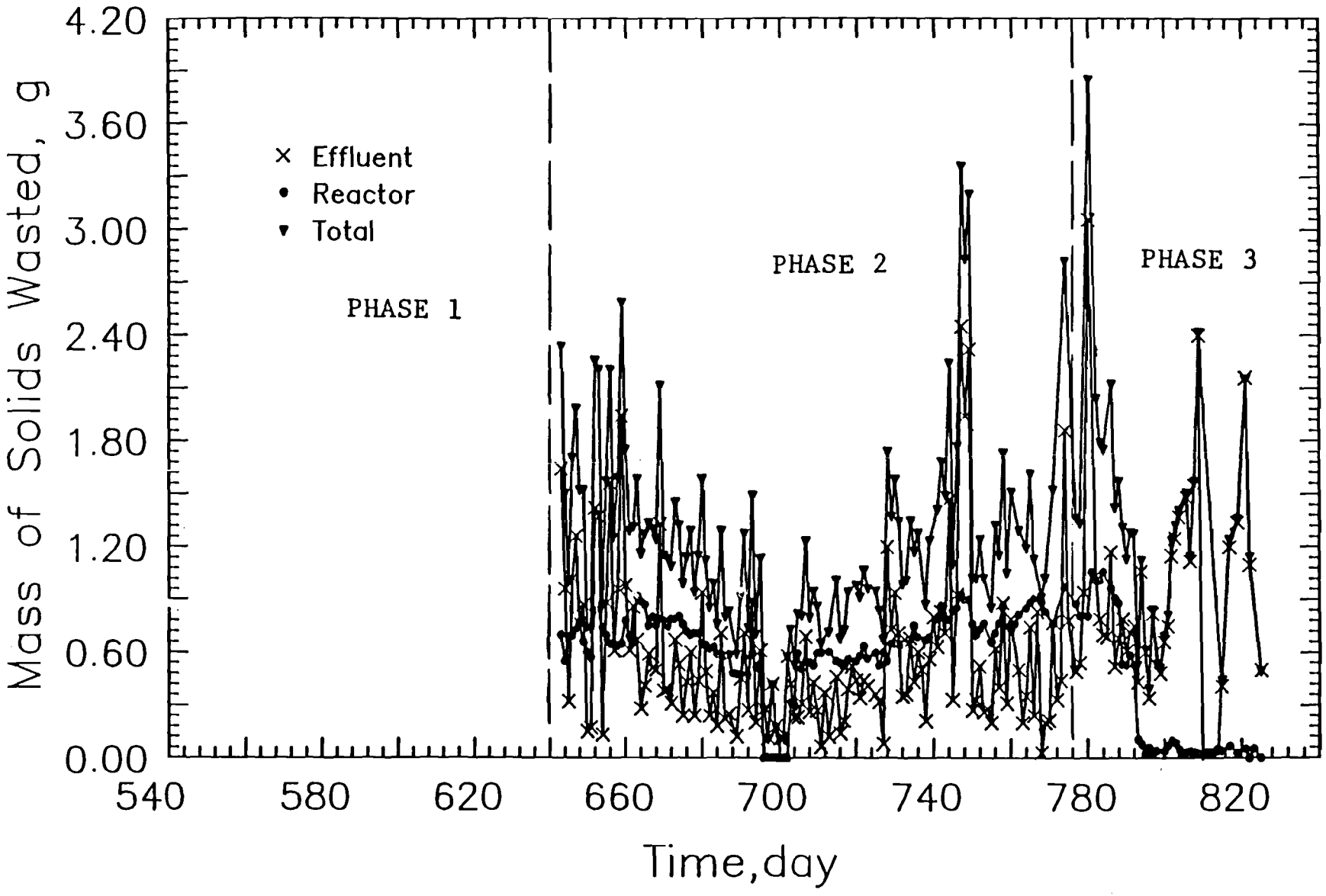

Fig. 23 Solid Wasted, Denitrification Reactor.

Figure 23. The concentration of total suspended solids lost in the effluent ranged between 5 and 380 mg/L (see Figure 24). The MCRT for this phase of operation is presented in Figure 25. During the period of Days 641-775, the MCRT ranged between 8 and 150 days, with an average of approximately 20 days.

During this phase of the operation, nitrate-nitrogen substrate limitation was imposed on the system, i.e., the nitrate flow rate (nitrification effluent) was maintained at a constant level but methanol was supplied at a decreased rate of 17.5 g/d. This rate corresponded to a ratio of 3.5 g methanol per g of nitrate-nitrogen, i.e., this ratio was deliberately chosen because it is in excess of theoretical ratio of 2.47 g methanol per g nitrate-nitrogen (McCarty et al.[36]). Due to the excess of methanol in the reactor, all the nitrate-nitrogen was removed from the effluent. The periods when nitrate-nitrogen was the limiting substrate, Days 657-675 and Days 736-752, are illustrated in Figures 21 and 22. During this substrate limitation, the concentrations of TOC in the influent and the effluent ranged between 450-750 mg/L and 50-250 mg/L, respectively (see Figure 22).

The second, and last, limitation imposed on the system during phase two of the operation, was a methanol limitation. The methanol feed pump was gradually reduced from 17.5 g/d to 10-12 g/d. This lower flow rate of methanol corresponded to a ratio of 2-2.4 g methanol/g nitrate-nitrogen. Since this ratio was below the theoretical ratio of 2.47 g methanol/g nitrate-nitrogen and these was less methanol available to the microorganisms to reduce the influent nitrate-nitrogen, the concentration of nitrate-nitrogen in the effluent increased. The periods for which methanol was the limiting substrate, i.e., Days 676-695 and 701-735, are illustrated in Figures 21 and 22. During this substrate limitation, nitrate-nitrogen concentration in the effluent increased from 0 to 250 mg/L, the TOC concentration in the influent was gradually reduced from 500 to 150 mg/L and the resulting effluent concentration dropped from 220 to 40 mg/L (see Figures 21 and 22).

Daily pH measurements of the system during phase 2 are presented in Figure 26. The pH of the synthetic feed was 7.0. The pH of the influent and the reactor during this phase of operation varied between 6.5 to 8.4 and 8.95 to 9.37, respectively. The pH of the effluent was almost the same as the pH of the reactor (i.e., 1-2% variation).

The alkalinity of the influent and the effluent is illustrated in Figure 27. During this phase of operation, the average values for the influent and the effluent alkalinity were 530 and 1510 mg/L as $CaCO_3$, respectively. The temperature of the reactor was maintained at ambient temperature and varied from 16 to 30°C (see Figure 28).

Phenol Substitution

During the last phase of the study, beginning on Day 776, methanol was replaced by phenol as the external carbon source and MCRT was maintained at approximately 20-day (see Figure 25). The amount of organic carbon required to reduce the nitrate-nitrogen was determined by performing a mass balance on the system and on a gradual basis, phenol was substituted for methanol. For example, during the initial period, if 4 g of organic carbon was needed to reduce 1 g of nitrate-nitrogen, 60% or 2.4 g of organ carbon was supplied as methanol and the rest, 40% of 1.6 g or organic carbon, was used as phenol. The phenol substitution steps for this phase of the operation were as follows:

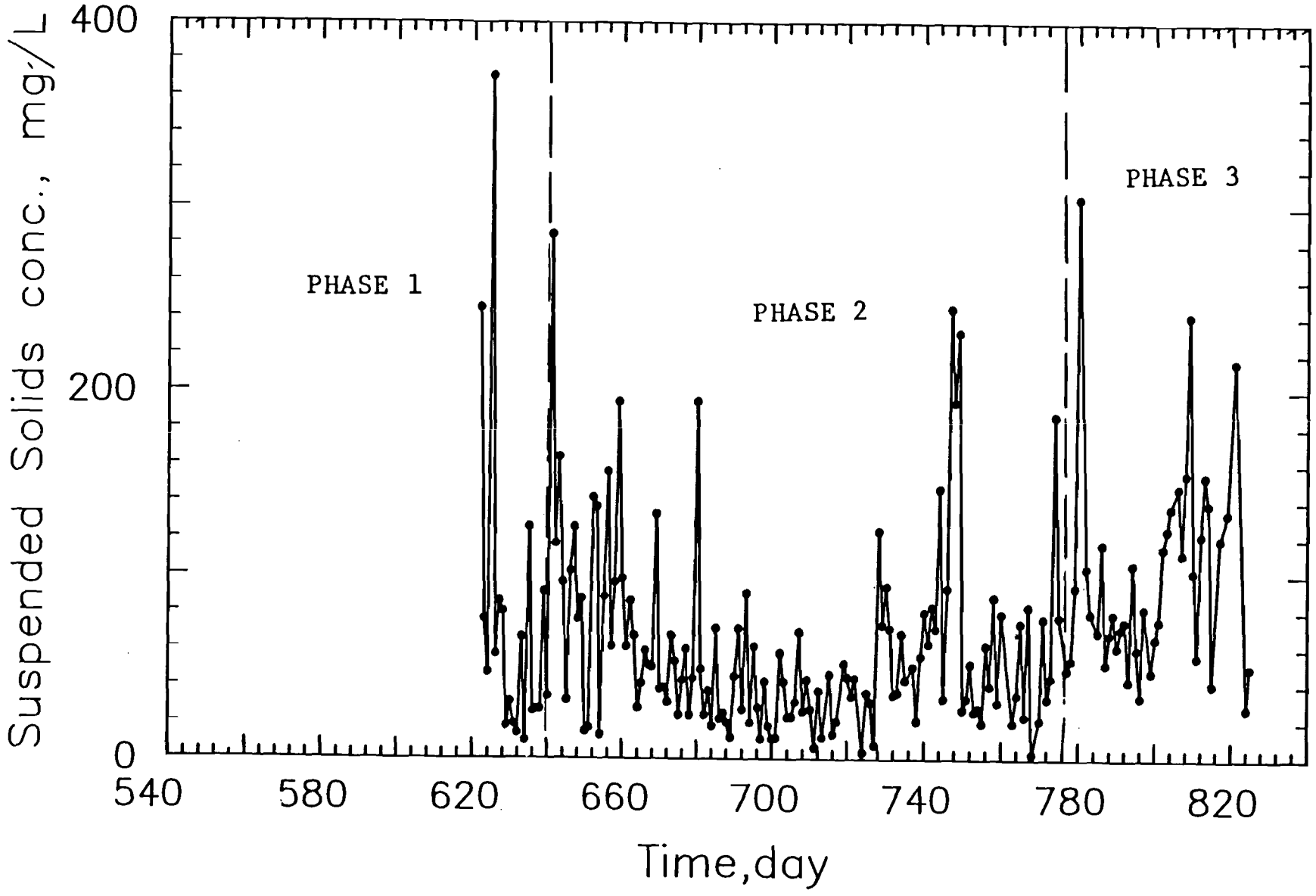

Fig. 24 Effluent Suspended Solids, Denitrification Reactor.

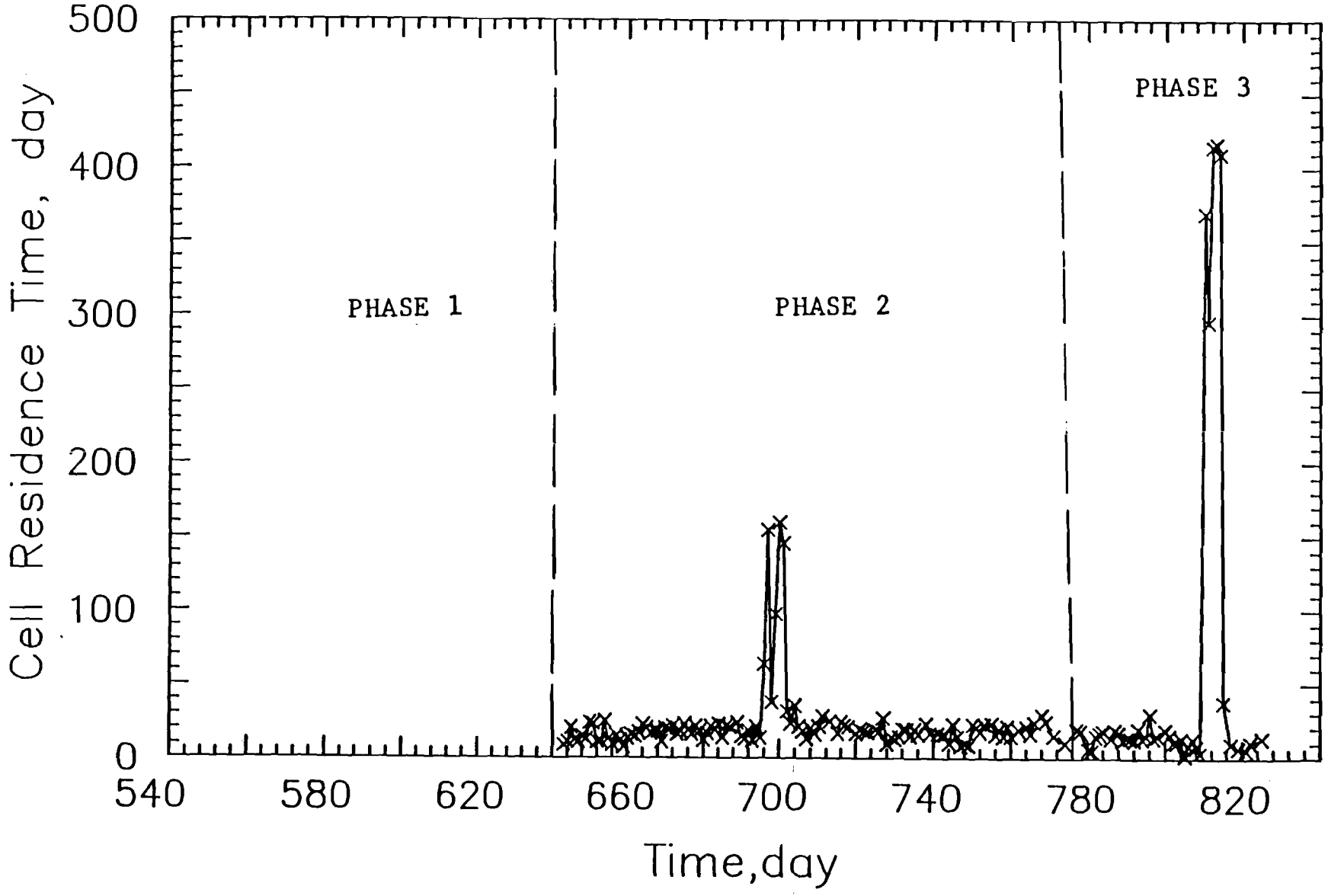

Fig. 25 Cell Residence Time, Denitrification Reactor.

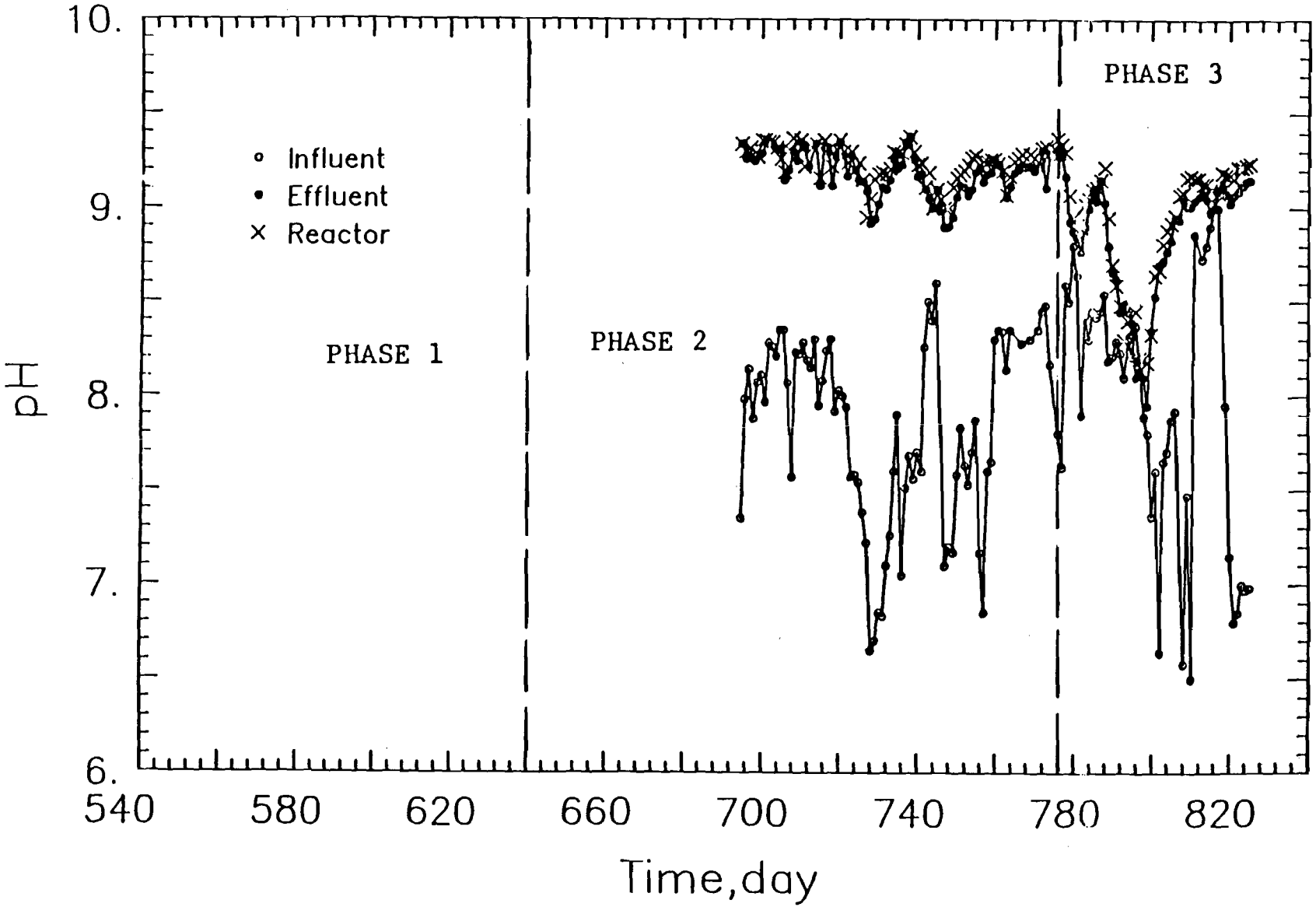

Fig. 26 pH, Denitrification Reactor.

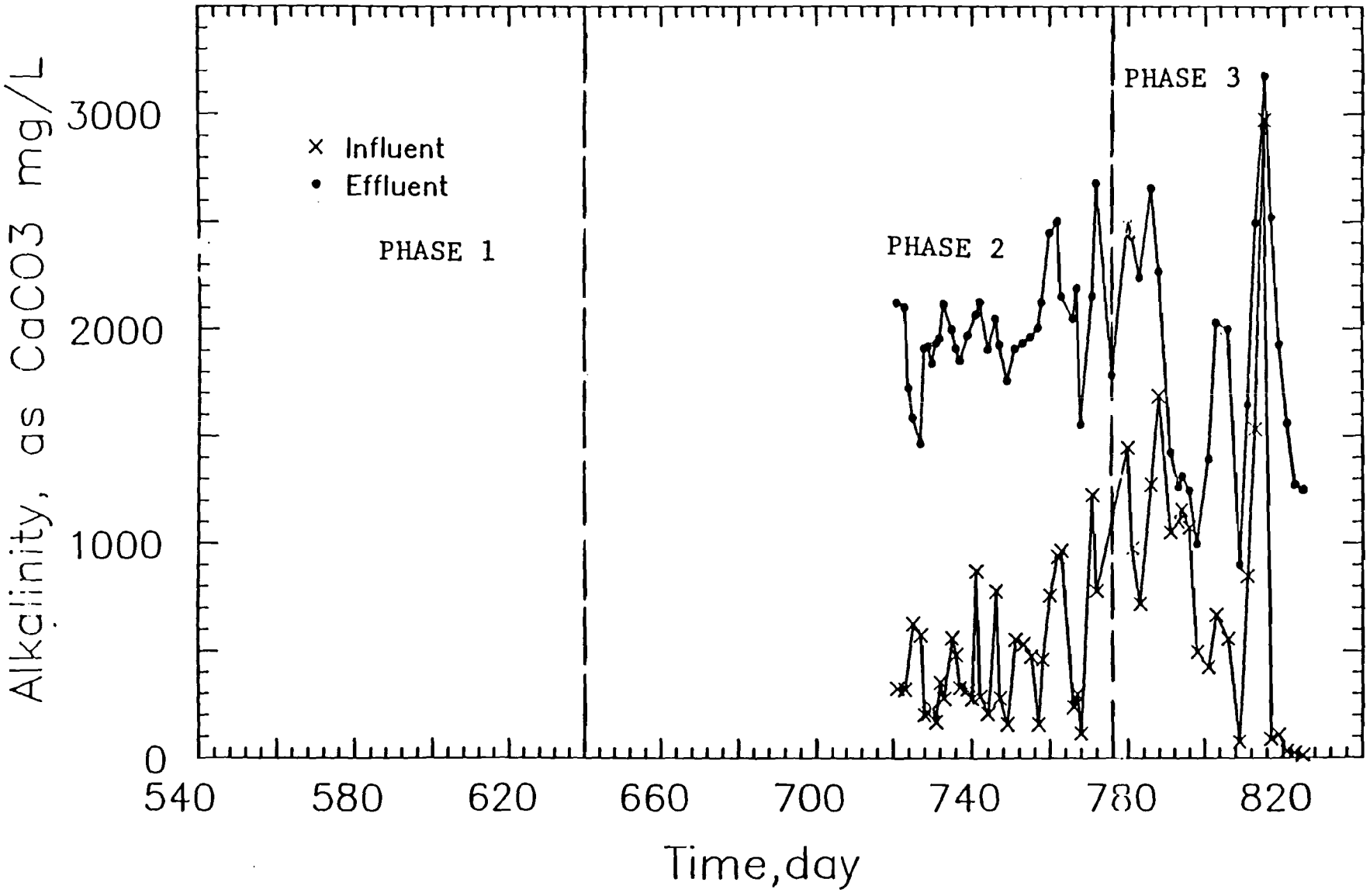

Fig. 27 Alkalinity, Denitrification Reactor.

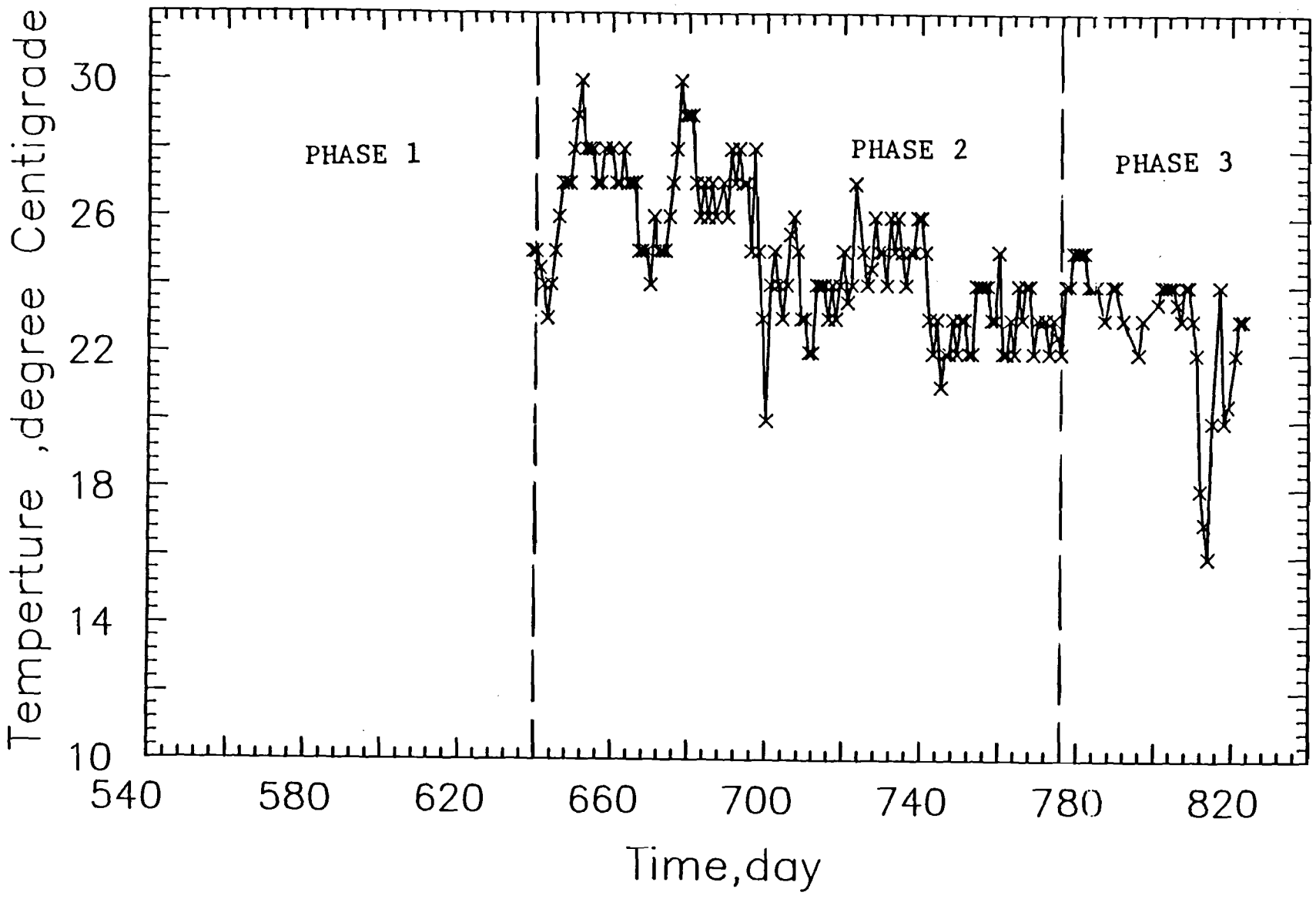

Fig. 28 Temperature, Denitrification Reactor.

1) 100% methanol-30% phenol; 2) 60% methanol-40% phenol; 3) 20% methanol-80% phenol; 4) 0% methanol-100% phenol; 5) 269% phenol; 6) 122% phenol; 7) 100% phenol; 8) 90% phenol-10% methanol; 9) 70% phenol-30% methanol; and, 10) 50% phenol-50% methanol. These substitutions of phenol for methanol are illustrated in Figure 29.

100% Methanol - 30% Phenol. In the first substitution step, the mass of organic carbon to reduce all the nitrate in influent was determined and 100% of that was supplied as methanol. Phenol was supplied as a 30% excess of organic carbon. This period lasted 6 days, beginning on Day 776. All influent nitrate-nitrogen was removed and the total mass of solids in the reactor remained relatively stable at 25-35 g (see Figure 20). The pH of the reactor varied between 8.95 and 9.37. The influent and effluent TOC concentrations were 1000 and 1400 mg/L, respectively.

60% Methanol - 40% Phenol. During the next 5 days, phenol was used as the organic carbon, and was supplied as 40% of the TOC required to reduce a unit mass of nitrate-nitrogen. The effluent concentration of nitrate-nitrogen remained unchanged, i.e., the concentration was almost zero. The pH of the reactor ranged between 8.95 and 9.37 and the influent and effluent TOC concentrations were 600-800 mg/L and 300-400 mg/L, respectively (Figures 26 and 22). The mass of solids in the reactor was approximately 25-35 grams.

20% Methanol - 80% Phenol. The mass of phenol was increased from 40% of the TOC to 80% of the TOC during Days 787-788. The performance of the system remained relatively unchanged, i.e., the pH, mass of solids, MCRT, and nitrate-nitrogen in the effluent remained stable.

100% Phenol. For the next three days, 789-791, phenol was used as the sold source of carbon. Due to this increase in phenol mass, the pH decreased to 8.6 and the mass of solids in the reactor decreased from 23 to 16 g. The concentration of nitrate-nitrogen in the effluent started increasing on Day 789 (Figure 21).

269% Phenol. For one day the mass of organic carbon added to reactor was increased by 269%, i.e., the organic carbon mass was increased from 6.8 to 18.3 g or the phenol mass was increased from 8.9 to 23.9 g.

The resulting pH of the reactor decreased to 8.2 and nitrate-nitrogen concentration increased to 200 mg/L in the effluent.

122% Phenol. For the next period, Days 793-794, the mass of organic carbon was reduced to 122%, i.e., the organic carbon mass was decreased from 18.3 to 8.3 g or phenol mass was decreased from 23.9 to 10.87 g. The resulting pH of the reactor was 8.7 and 8.6 during these two days.

100% Phenol. During the next three days, 795-797, the mass of organic carbon was reduced by 22.0%, i.e., the mass of organic carbon was decreased from 8.3 to 6.8 g or phenol mass was reduced from 10.87 to 8.9 g. The concentration of nitrate-nitrogen in the effluent increased to 380 mg/L and the pH of the reactor was about 8.4.

10% Methanol - 90% Phenol. For Day 798, 10% of the TOC was supplied as methanol and the rest as phenol, i.e., 0.68 and 6.12 g of carbon as methanol

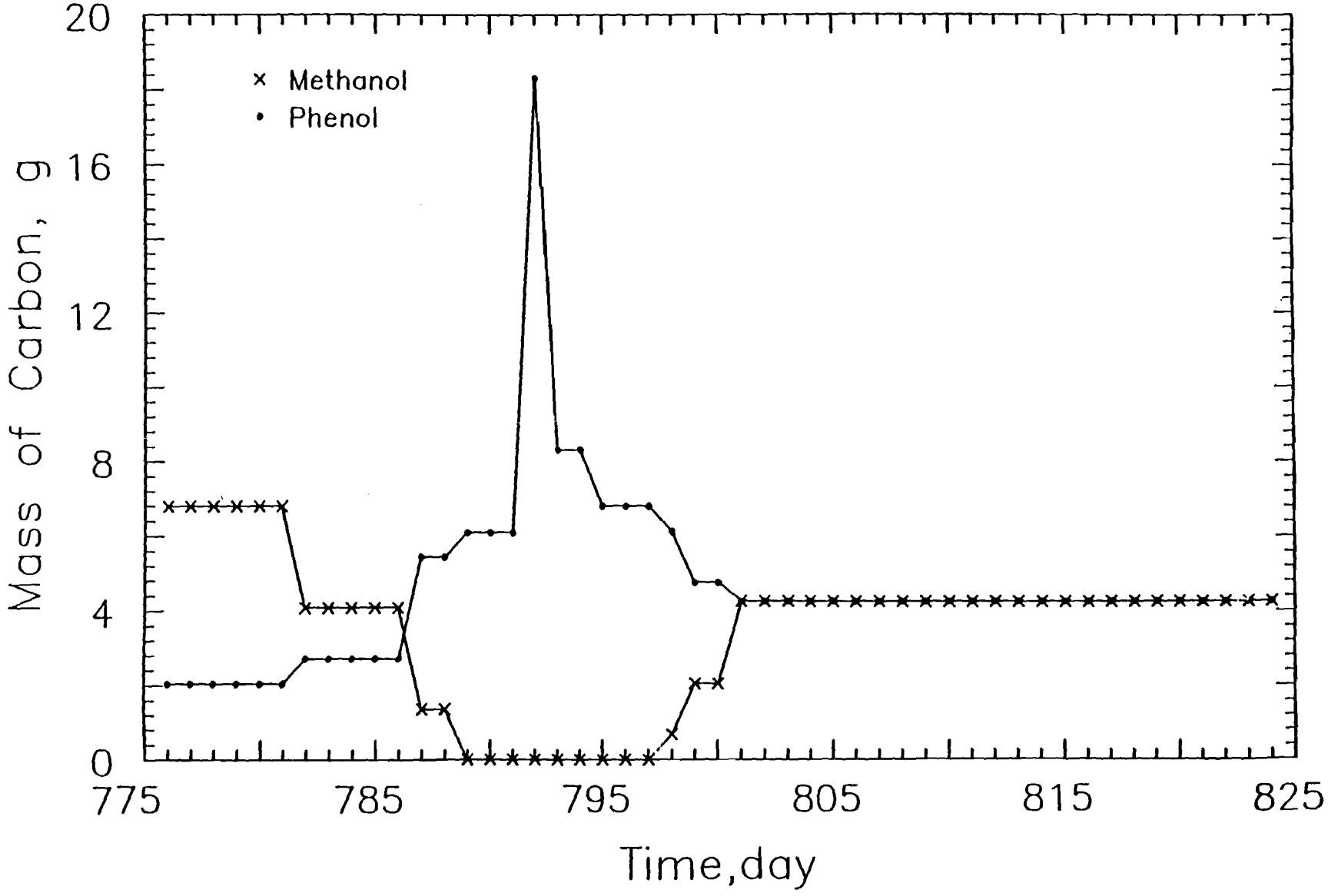

Fig. 29 Carbon Feed - Phase 3 - Denitrification Reactor.

and phenol, respectively. The nitrate-nitrogen concentration in the effluent remained above 300 mg/L.

30% Methanol - 70% Phenol. During the Days 799-800, 30% of the TOC was supplied as methanol and the rest as phenol, i.e., 2.04 and 4.76 g of carbon as methanol and phenol, respectively. The nitrate-nitrogen concentration in the effluent decreased to 290 mg/L.

50% Methanol - 50% Phenol. During the next twenty-five days, beginning on Day 801, 50% of the TOC was supplied as methanol and the rest as phenol, i.e., 4.25 g of carbon as phenol and methanol. At the beginning of this period the concentration of influent to the anaerobic filter was increased, and as a result the nitrate-nitrogen concentration of the influent increased from 500-550 to 700-750 mg/L and consequently the organic carbon concentration increased to 800-900 mg/L.

The pH of the reactor steadily returned to a range of 9-9.2 and the nitrate-nitrogen concentration in the effluent was reduced to 100 mg/L due to decrease in the influent nitrate-nitrogen concentration. However, as the influent nitrate-nitrogen concentration increased to 700 mg/L the effluent concentration increased to 300-400 mg/L. Daily pH measurements of the system during Phase 3 is presented in Figure 26. The pH of the influent and reactor varied between 6.5 - 9.0 and 8.2 - 9.25, respectively. Daily alkalinity measurements of the system during Phase 3 are presented in Figure 27. The alkalinity of the influent and effluent varied between 300-2900 and 900-3200 mg/L as $CaCO_3$, respectively. The temperature of the reactor ranged from 16 to 26 °C and is presented in Figure 28.

CONCLUSIONS

Based on the results from the suspended growth denitrification of the anaerobically treated-nitrified coal gasification wastewater, the following conclusions are made.

1. Suspended growth denitrification using methanol with cell recycle can be used to remove virtually 100% of the nitrate-nitrogen from anaerobically treated and nitrified coal-gasification wastewater.

2. The anaerobically treated and nitrified coal gasification wastewater had an insignificant amount of TOC, therefore, it was necessary to use an external carbon source, e.g., methanol, to reduce nitrate in the nitrified coal gasification wastewater.

3. One-hundred percent removal of nitrate-nitrogen was achieved at a ratio of 2.45 g of methanol per g of nitrate-nitrogen, a 20-day cell residence time, a 24-hour hydraulic retention time; the pH of the reactor ranged between 8.95-9.35 during this operation.

4. The pH of the nitrification effluent in the range of 6.0-8.5 had an insignificant effect on the denitrification performance, i.e., the nitrate removal did not change.

5. The pH of the reactor and alkalinity production were directly related to the nitrate-nitrogen and methanol concentration in the influent, i.e., high

concentration in the influent resulted in more production of hydroxide ion and alkalinity.

6. Increasing the methanol flow rate resulted in instantaneous reduction in the nitrate concentration in the influent or vice versa.

7. Phenol can be partially substituted for methanol as the external carbon source. However, the inhibitory effect of phenol was observed when 100% phenol was used at a concentration of 600-700 mg/L. As a result the nitrate removal was reduced to 20-30% and the pH decreased to 8.2-8.3.

INHIBITION STUDY

Serum Bottle inhibition studies were carried out utilizing the mixed liquor from an active anaerobic activated carbon reactor and ten compounds found in coal gasification effluent at relatively high concentrations. Table 12 summarizes the results of the study, while Figures 30 and 31 show the results of the addition of phenol and raw wastewater to the mixed liquor.

As can be seen in Figures 30 and 31 the addition of phenol or raw wastewater does not appear to cause any inhibition of gas production.

Figures 32, 33, and 34 show that the addition of hydantoins to the mixed liquor do not inhibit gas production and the sample containing the additional substrate produce more gas than these without the additional substrate.

The addition of the cresol isomers had no effect on the gas production, indicating no inhibition. However, the addition of any of the picolines caused complete cessation of gas production indicating either severe inhibition and/or toxicity.

Continuous Flow Anaerobic Activated Carbon Filter Treatment of Pretreated Wastewater

In conjunction with the serum bottle inhibition studies an activated carbon filter was operated with dilute pretreated wastewater as the feed. The system was operated for a period of 200 days with limited success. Figure 35 shows the performance of the filter in terms of TOC removal. Although the feed substrate was primarily hydantoins from the pretreated wastewater, only 40 to 60% of the TOC was removed and gas production during the entire period averaged less than 1 L/d. Although extensive efforts were expended in searching for gas leaks, none were found indicating that the predominant removal mechanism was apparently physical adsorption of the hydantoins onto the granular activated carbon. Total hydantoin removal averaged approximately 60% during the period.

Table 12. Gas Production Inhibition by Coal Gasifier Effluent Constituents

Compound	Concentration mg/L	Results
phenol	280	No inhibition
o-cresol	150	No inhibition
m-cresol	150	No inhibition
p-cresol	150	No inhibition
hydantoin	200	No inhibition
5,5-dimethylhydantoin	800	No inhibition
5-methyl-5-ethylhydantoin	260	No inhibition
2-picoline	25/75	Complete inhibition
3-picoline	25/75	Complete inhibition
4-picoline	25/75	Complete inhibition

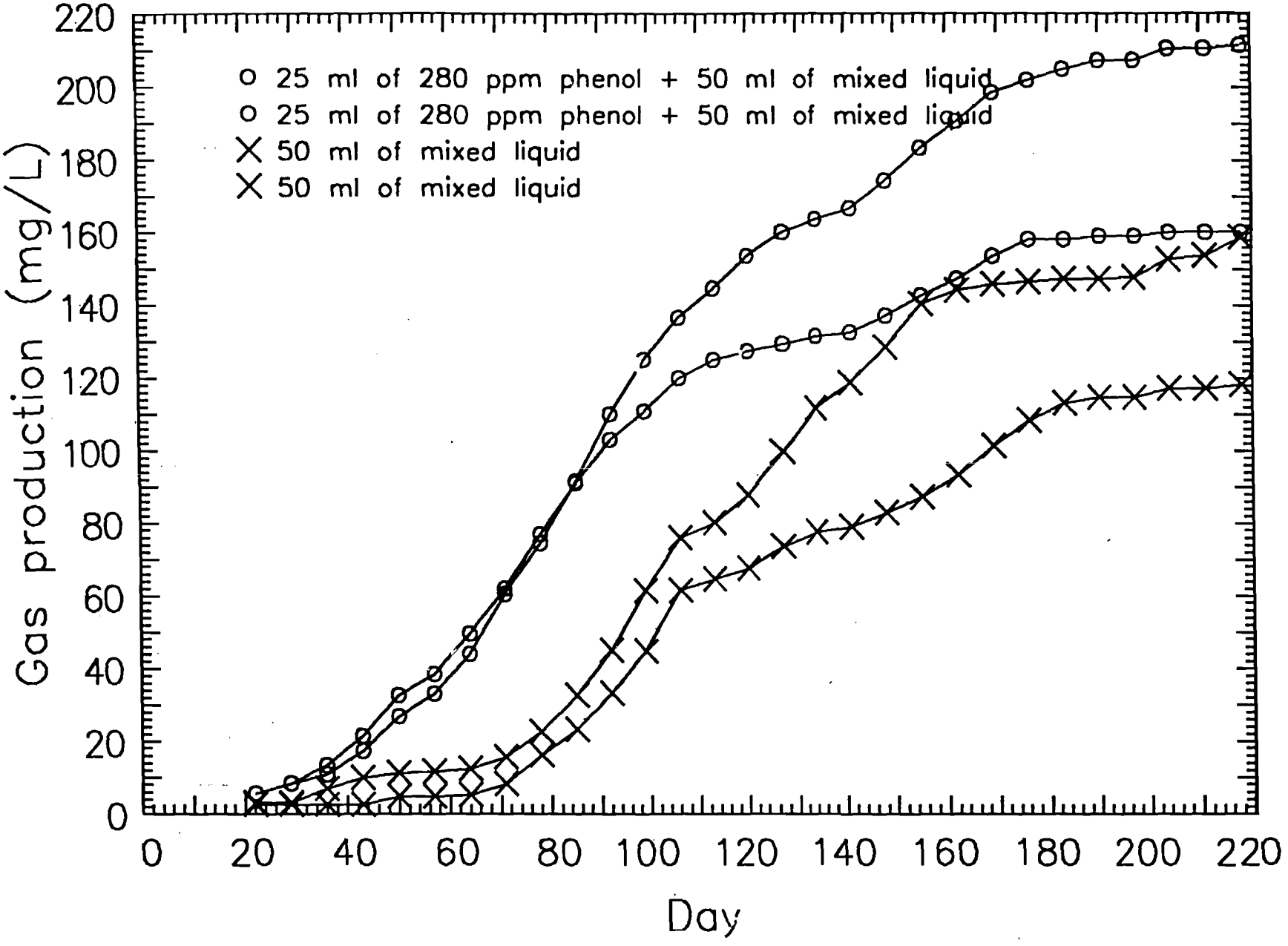

Fig. 30 Effect of Phenol on the Degradation of Coal Gasifier Effluent.

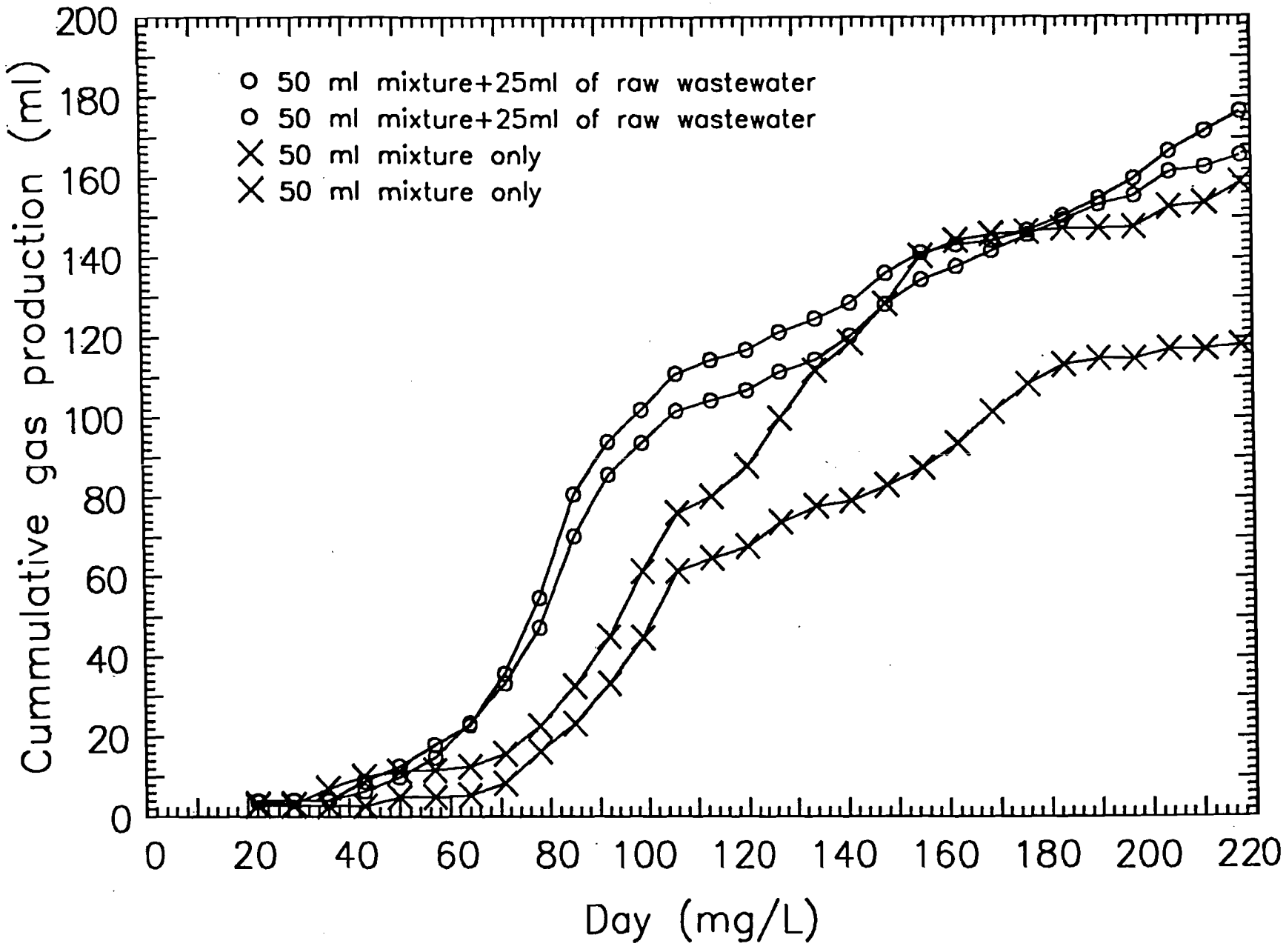

Fig. 31 Effect of Coal Gasification Wastewater on Gas Production.

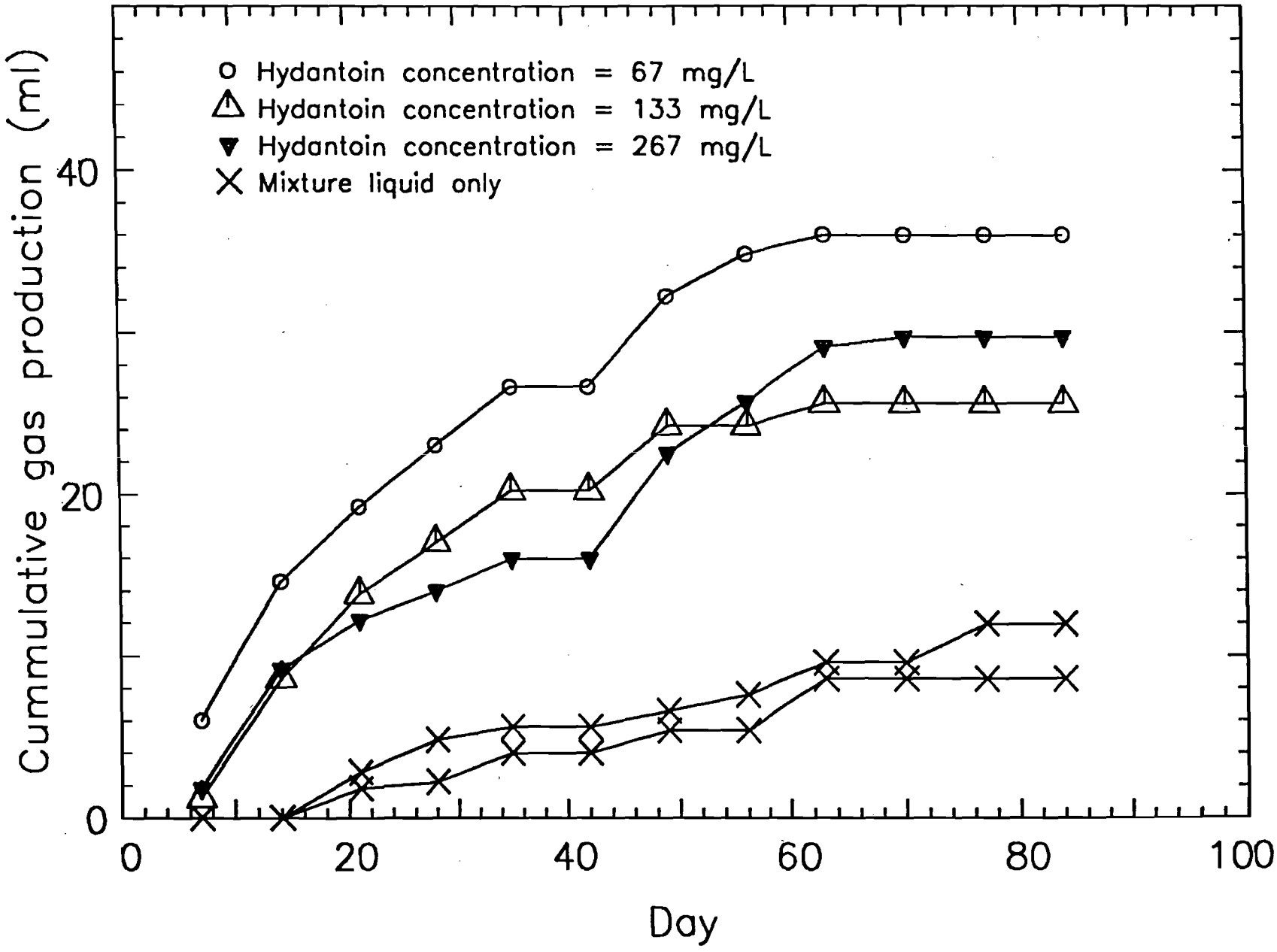

Fig. 32 Effect of Hydantoin on Gas Production.

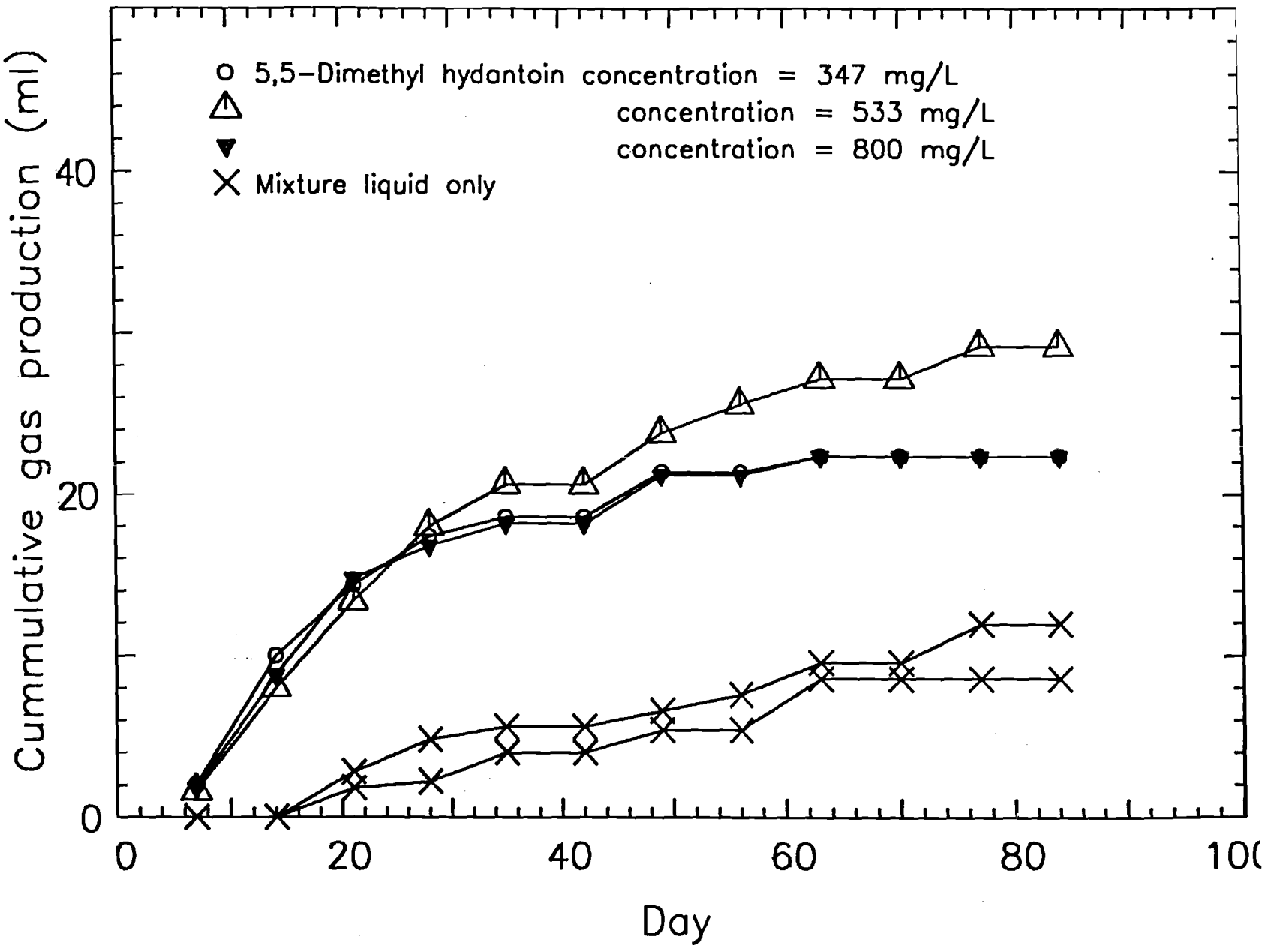

Fig. 33 Effect of 5,5-Dimethyhydantoin on Gas Production.

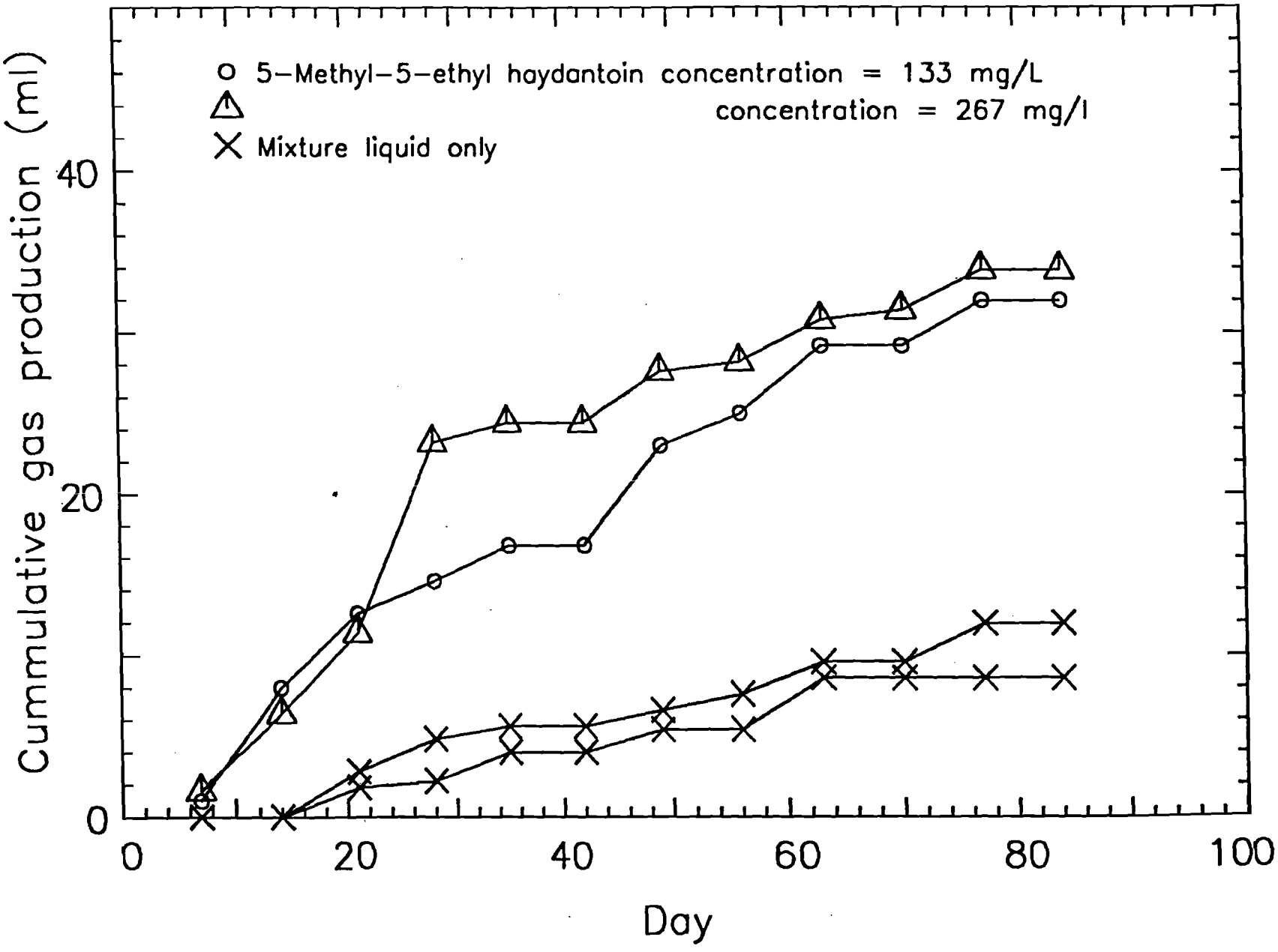

Fig. 34 Effect of 5-Methyl-5-Ethylhydantoin on Gas Production.

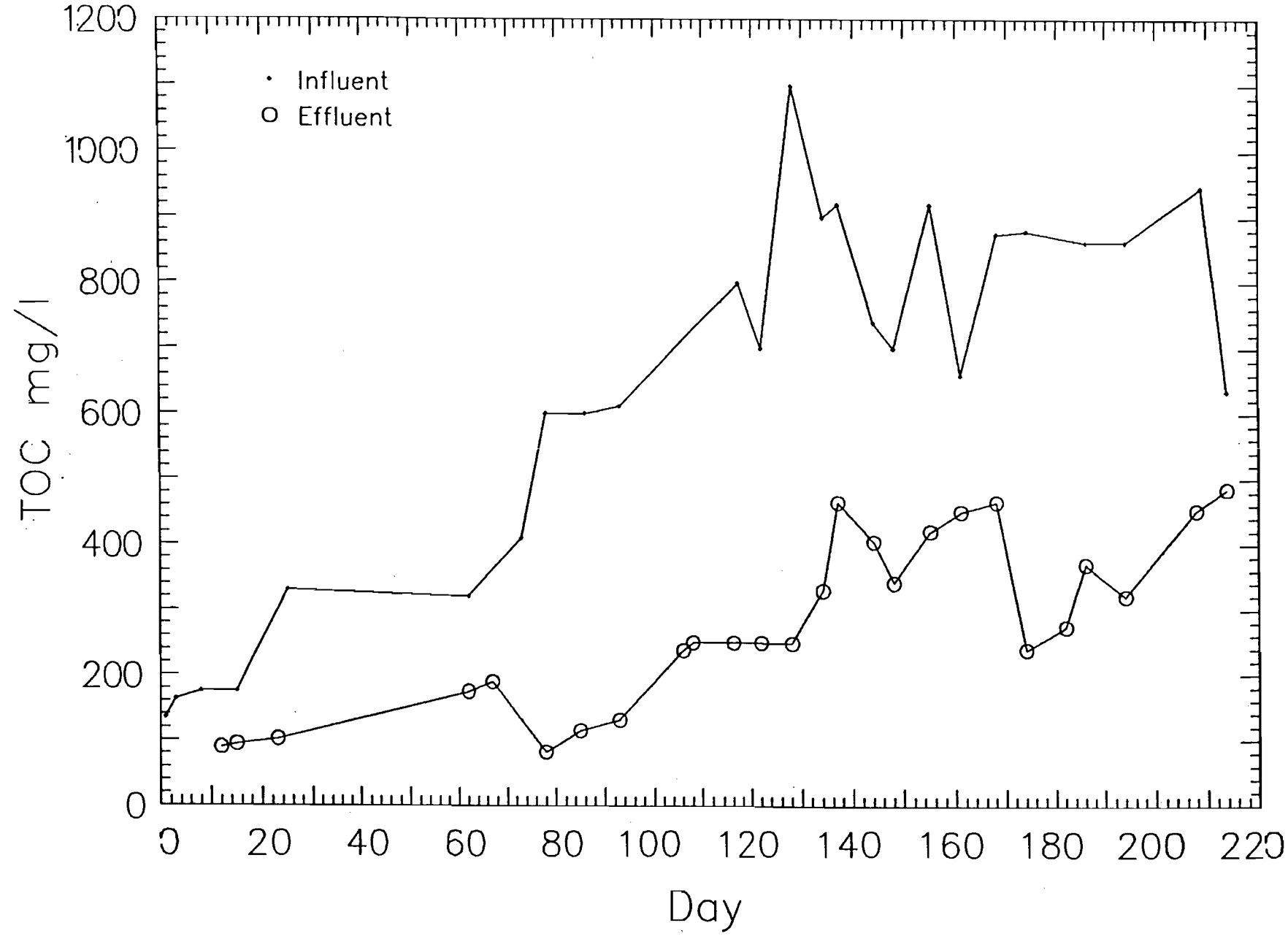

Fig. 35 Total Organic Carbon Removal, Pretreated Wastewater.

HYDANTOIN ADSORPTION STUDIES

Batch Kinetic Tests. The results of the single solute batch kinetics tests are shown in Figures 36, 37, and 38. The initial conditions are shown in Table 13.

The batch kinetic study for hydantoin showed a C_o value of 450 mg/L which decreased to 395 mg/L, the equilibrium concentration, in a 1.5 hour time span. In fact, 85% of the adsorption by the activated carbon occurred in the first 20 minutes of the experiment. The same basic sequence occurred for the other two solutes. The batch kinetic tests for 5,5-dimethylhydantoin with a C_o of 500 mg/L reach equilibrium concentration after 3 hours, as did the 5-ethyl-5-methylhydantoin with the same initial concentration. Most of the adsorption of both solutes also occurred in the first 20 minutes of the test.

From the batch kinetic test results, the adsorption of the hydantoins were very rapid. Equilibrium was definitely reached after 3 hours for each compound and, therefore, three hours would be the minimum elapsed time required to ensure that equilibrium concentration is reached. The temperature at which the tests were performed was 24-25°C.

Isotherm Tests. The results of the isotherm tests are shown in Figures 39, 40, and 41. The initial conditions are shown in Table 14.

The isotherms for hydantoin and 5,5-dimethylhydantoin were very similar with the only difference being a slight increase in curvature for the 5,5-dimethylhydantoin isotherm over the hydantoin with equilibrium concentrations in excess of 10 mg/L. The X/m values for a given equilibrium concentration were also very similar. The isotherm for 5-ethyl-5-methylhydantoin was much different from the other two solutes. Overall, there was a higher X/m value for any given equilibrium concentration indicating an adsorption preference for 5-ethyl-5-methylhydantoin over the single solutes. In examining all three curves as a whole, there appears to be a systematic transition in curvature in concentrations in excess of 10 mg/L from hydantoin to 5-ethyl-5-methylhydantoin. Also shown are the results of the bisolute and trisolute isotherm points. Each point represents the X/m and equilibrium concentration found for a given solute in competition with the labelled solute. For instance, in Figure 39, which is the isotherm for hydantoin, the point labelled 5,5 D represents the X/m value found for hydantoin in the bisolute hydantoin/5,5-dimethylhydantoin isotherm point. The point labelled trisolute represents the X/m value for hydantoin in the trisolute isotherm point. As can be expected, competition tends to reduce the amount of adsorbate adsorbed for a given equilibrium concentration. The relative affinity for the various solutes is also indicated by the fact that less hydantoin was adsorbed when in competition with 5-ethyl-5-methylhydantoin than when in competition with 5,5-dimethylhydantoin. When in competition with two different solutes, the amount adsorbed is even less. Since there are only a finite number of adsorption sites available, it was reasonable to assume that the increased competition between solutes in the trisolute isotherm point caused less of the individual solutes to be adsorbed than would be the case for the single or bisolute isotherm point.

In comparing each of the bisolute isotherm points, it appears that the relative affinity of activated carbon is in the order of hydantoin <

Table 13. Initial Conditions - Batch Kinetic Tests

hydantoin	
temperature	24°C
C_o	450 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2
5,5-dimethylhydantoin	
temperature	24°C
C_o	500 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2
5-ethyl-5-methylhydantoin	
temperature	25°C
C_o	500 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2

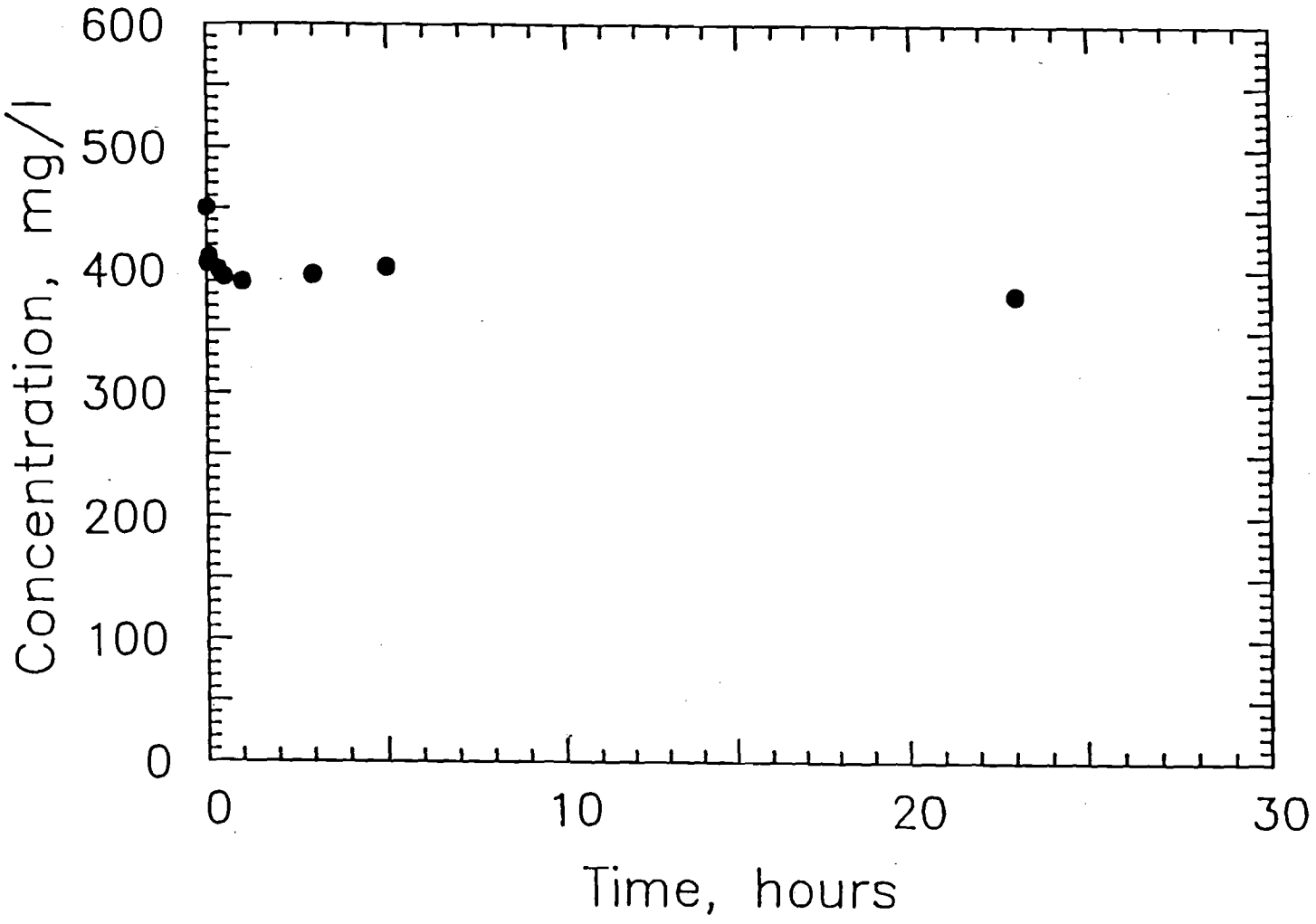

Fig. 36 Batch Kinetic Curve - Hydantoin.

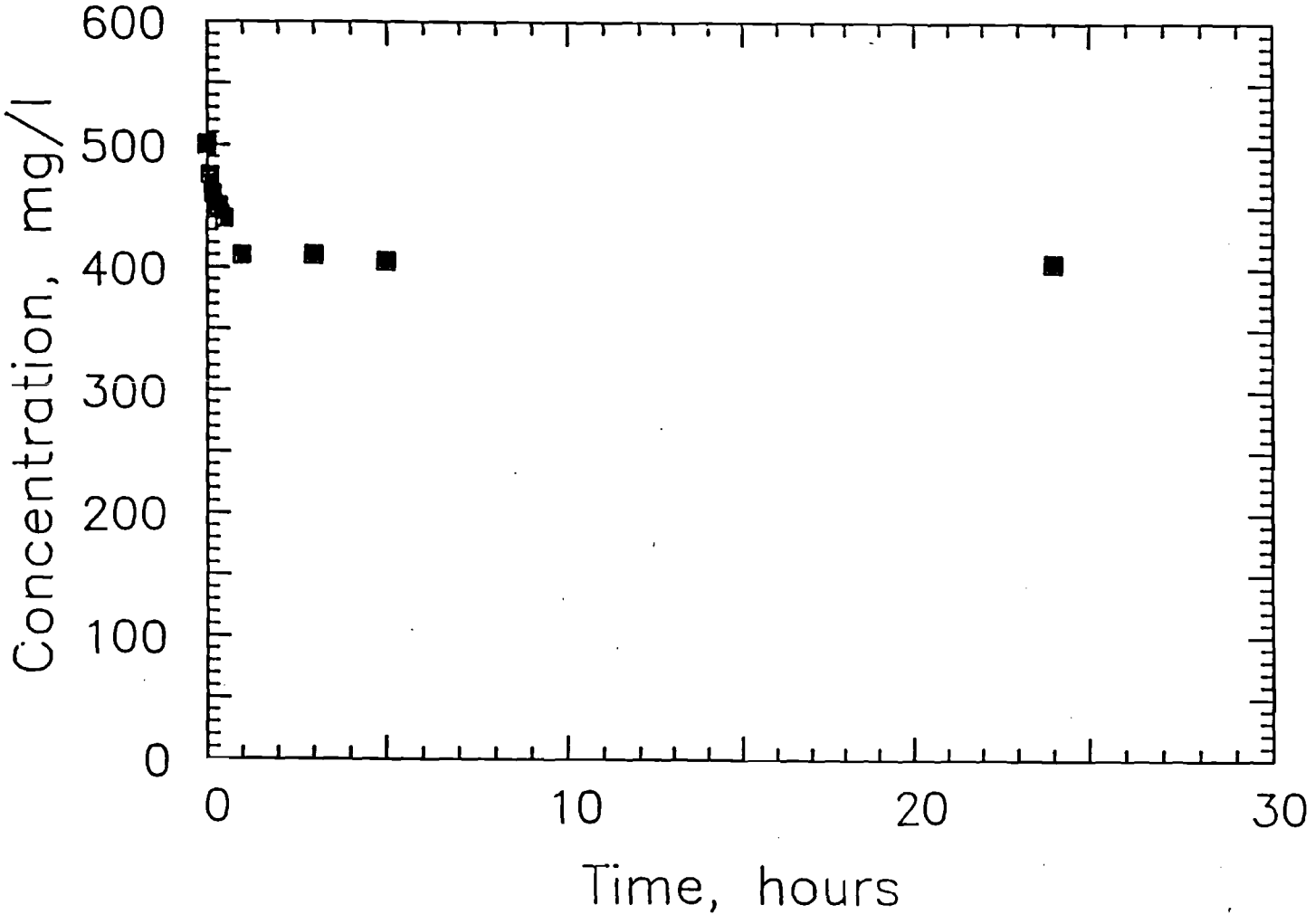

Fig. 37 Batch Kinetic Curve - 5,5-Dimethylhydantoin.

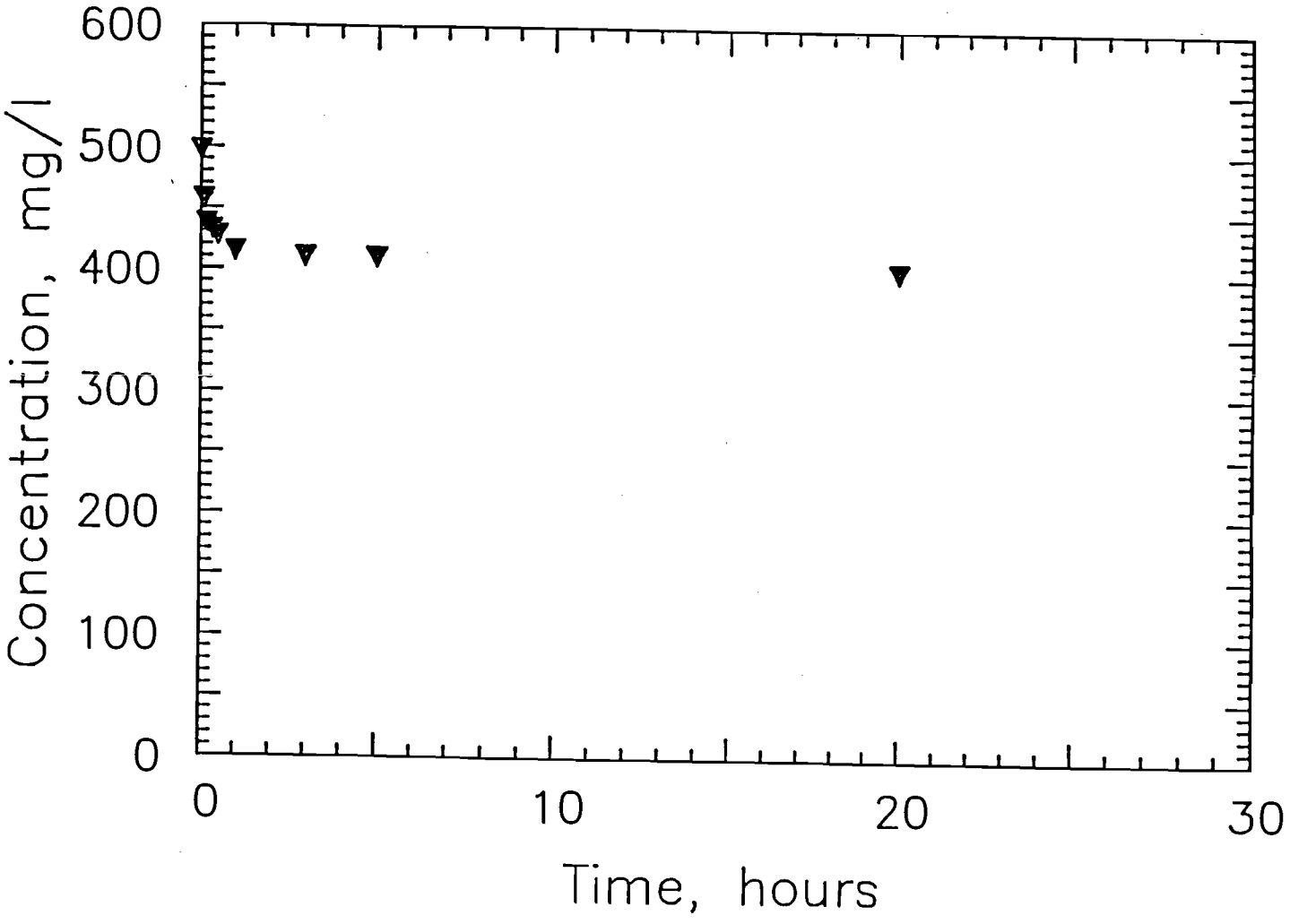

Fig. 38 Batch Kinetic Curve - 5-Methyl-5-Ethylhydantoin.

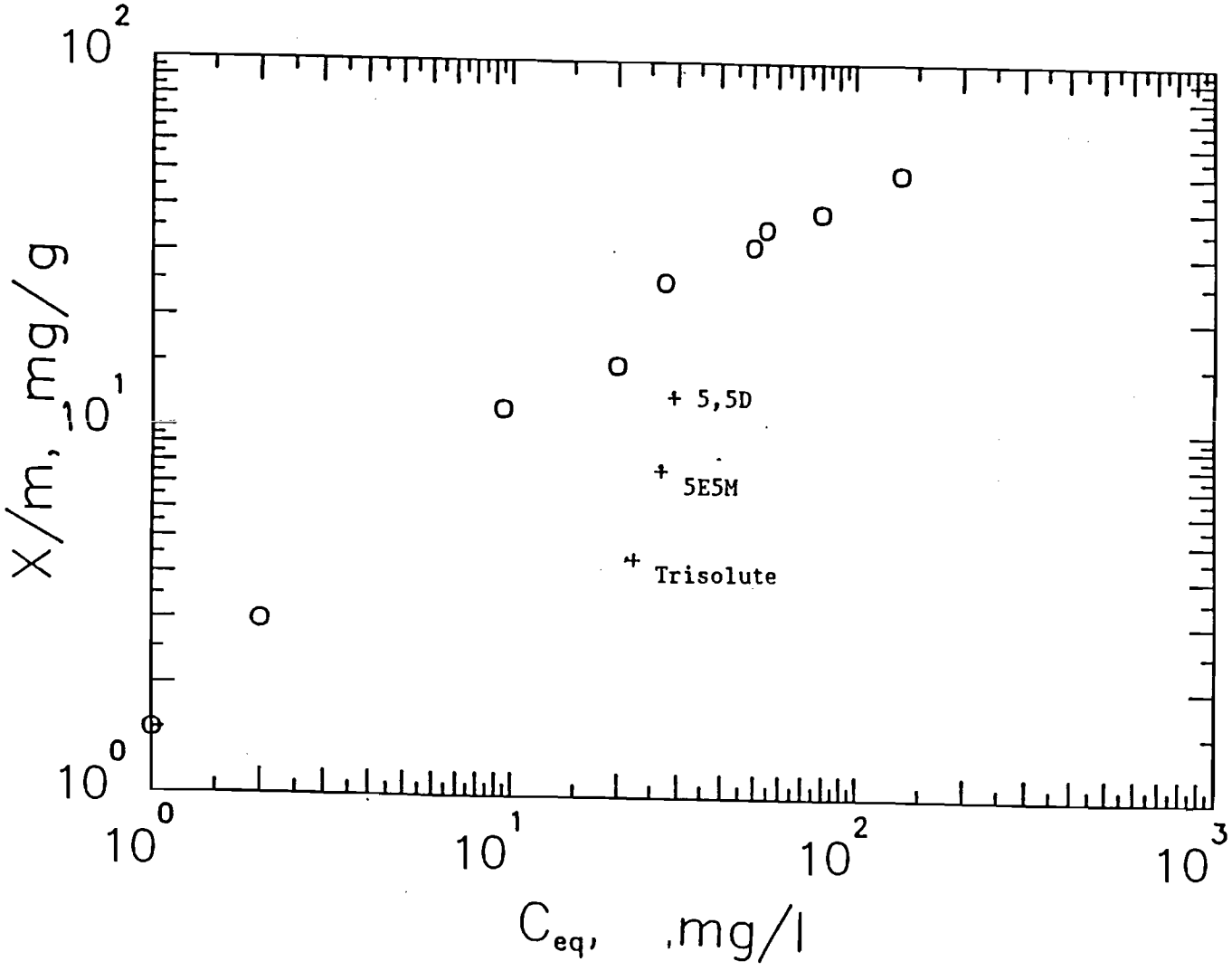

Fig. 39 Adsorption Isotherm - Hydantoin.

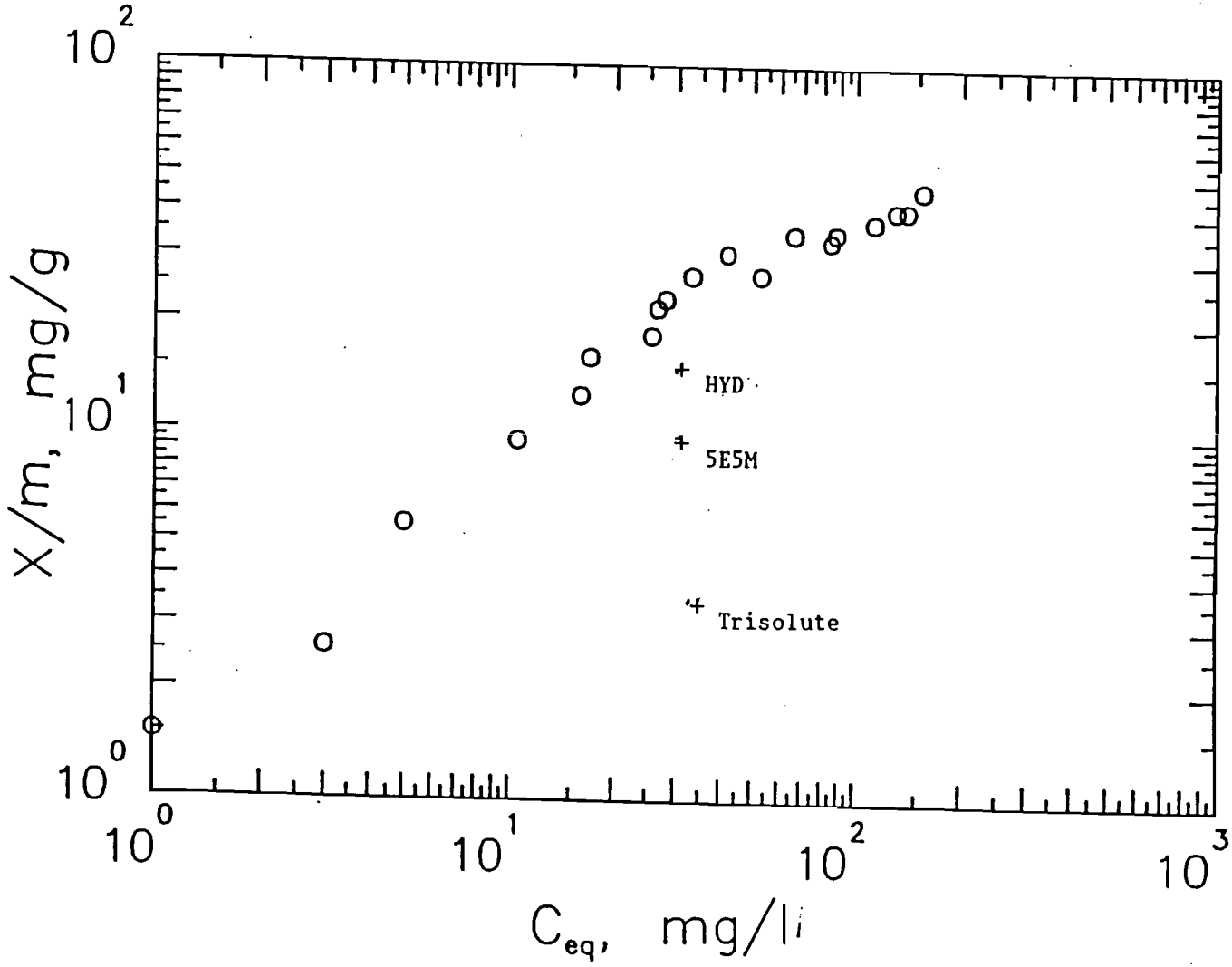

Fig. 40 Adsorption Isotherm - 5,5-Dimethylhydantoin.

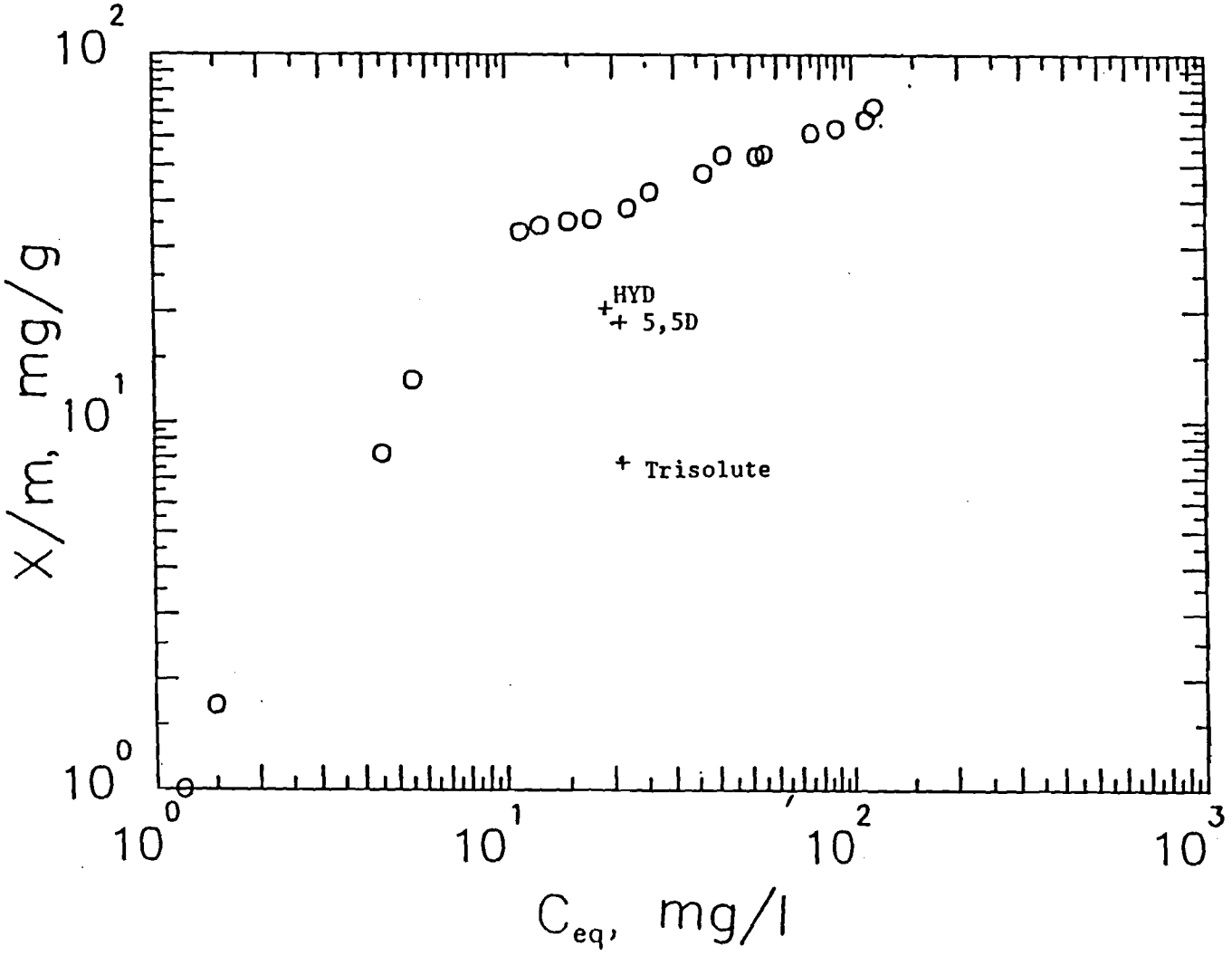

Fig. 41 Adsorption Isotherm - 5-Methyl-5-Ethylhydantoin.

Table 14. Initial Conditions - Isotherm Tests

Single solute	
temperature	28°C
C_o	various
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2
Bisolute	
temperature	28°C
C_o	50 mg/L each
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2
Trisolute	
temperature	28°C
C_o	50 mg/L each
carbon	2.5 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2

5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin.

The curvature found in the adsorption isotherms represents a departure from the strict Freundlich equation at equilibrium concentrations over approximately 10 mg/L. Therefore, some of the assumptions on which the Freundlich equation are based are invalid for the case in hand. Such assumptions were: 1) exponential distribution of adsorption energies; 2) one adsorbate molecule per adsorption site; 3) no surface transmigration of solute molecules; and, 4) monolayer adsorption. The three assumptions may or may not be valid, but is is probable that monolayer adsorption was still occurring at the highest equilibrium concentration tested.

pH Tests. The results of the high, medium, and low isotherm points with pH adjusted to values of 4, 7, and 9 are shown in Figures 42, 43, and 44. The initial conditions for each of the three solutes are shown in Table 15.

The isotherm points with pH adjusted to 4 and 7 provided equal X/m values for all three solutes at the medium and high concentration points. The variation in X/m values at the low isotherm points were small and probably due to experimental error. Of consequence were the X/m values of the isotherm points with the pH adjusted to 9. These points have X/m values significantly lower than the single solute curve and the X/m values at pH 4 and 7. Therefore, less solute is adsorbed at pH 9 than at a pH of 4 or 7.

Column Studies. The initial conditions for the column studies are shown in Table 16.

The results of the single solute column studies are depicted in Figures 45, 46, and 47. To provide a meaningful basis for comparison of the relative adsorption preferences of the three solutes, a calculation of the X/m values, Table 17, (amount of solute adsorbed per unit weight of carbon) reveals the following:

The X/m value for hydantoin is slightly higher than expected. However, if the X/m value of 41.3 mg/g with a C_{eq} of 55 mg/L is plotted on the single solute isotherm for hydantoin (Figure 39), it will be seen to be within experimental error. The X/m values for the other two solutes plot directly on the single solute curves (Figures 40 and 41). From the single solute column studies, it is readily apparent that 5-ethyl-5-methylhydantoin is more strongly adsorbed than the other two adsorbents.

More vivid evidence for the various affinities of the carbon for the different solutes was provided by the bisolute and trisolute breakthrough curves which are shown in Figure 48, 49, 50 and 51. The calculated X/m values for the bisolute and trisolute breakthrough curves are shown in Table 18.

Although from Figure 41 it appeared that the affinity of the carbon for hydantoin and 5,5-dimethylhydantoin was equal, the X/m values for the hydantoin/5,5-dimethylhydantoin in Table 18 showed that the carbon had a higher capacity for 5,5-dimethylhydantoin over hydantoin. The bisolute curve hydantoin/5-ethyl-5-methyl-hydantoin (Figure 49) showed a stronger adsorption of 5-ethyl-5-methylhydantoin by the fact that hydantoin was displaced from the activated carbon during the column test. This was demonstrated by the effluent concentration of the hydantoin becoming greater than the influent

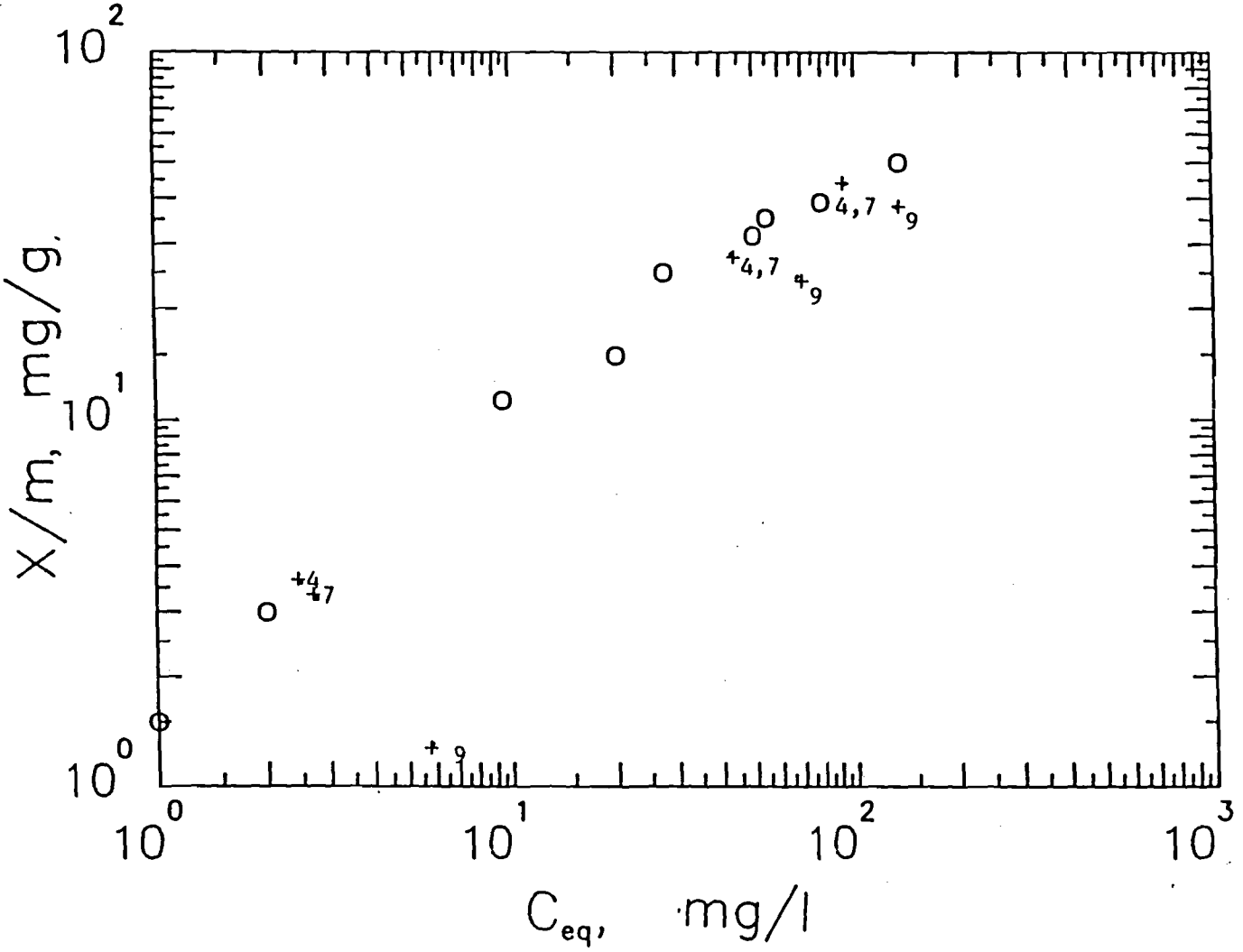

Fig. 42 Isotherm - pH Plot - Hydantoin.

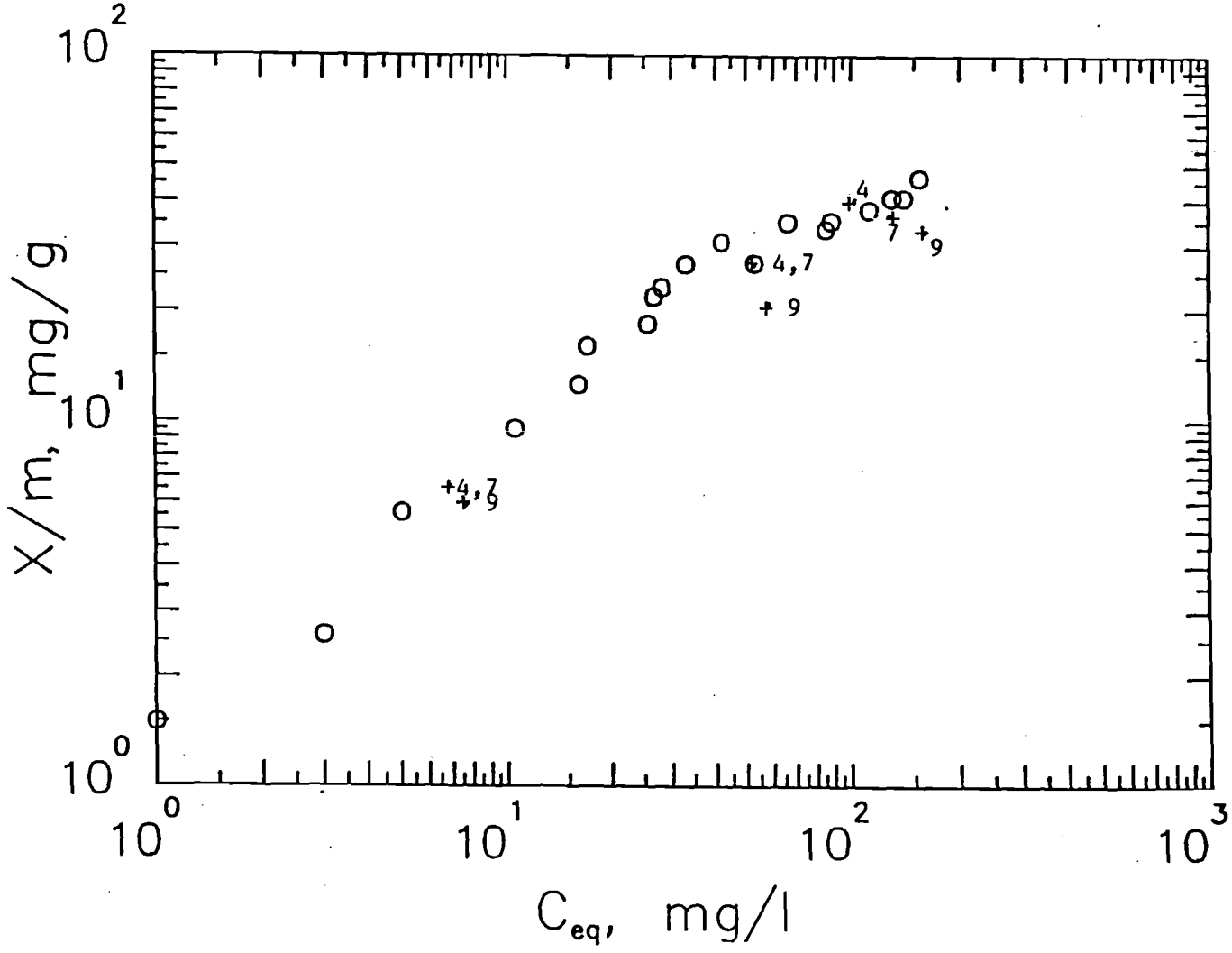

Fig. 43 Isotherm - pH Plot - 5,5-Dimethylhydantoin.

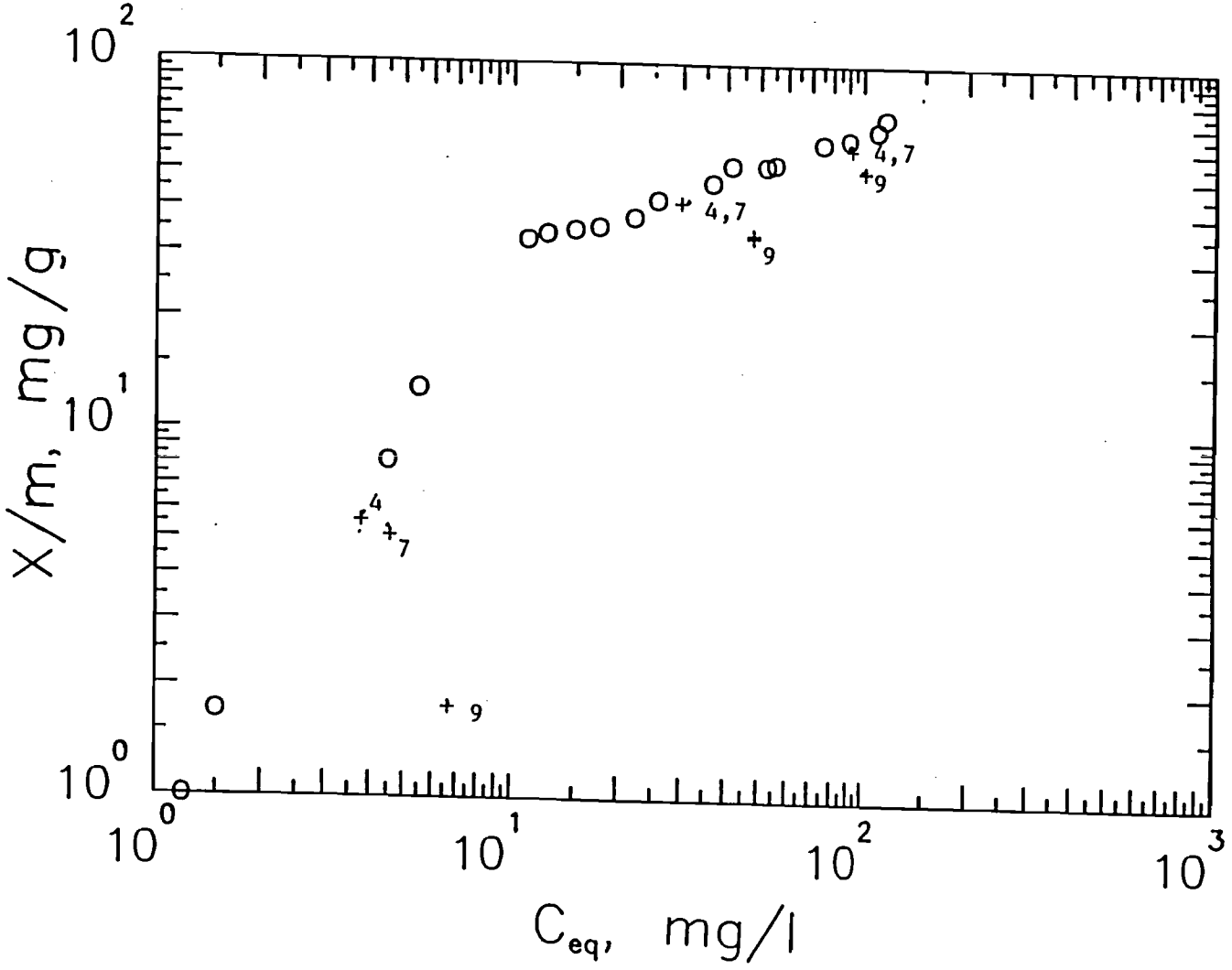

Fig. 44 Isotherm - pH Plot - 5-Methyl-5-Ethylhydantoin.

Table 15. Initial Conditions - pH Tests

Temperature	28°C
C_o	50 mg/L
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	4, 7, 9

Table 16. Initial Conditions - Column Studies

hydantoin		
temperature		28°C
influent concentration		55 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5,5-dimethylhydantoin		
temperature		28°C
influent concentration		45 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5-ethyl-5-methylhydantoin		
temperature		28°C
influent concentration		50.5 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
hydantoin/5,5-dimethylhydantoin		
temperature		28°C
influent	hydantoin	40 mg/L
	5,5-dimethylhydantoin	59 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
hydantoin/5-ethyl-5-methylhydantoin		
temperature		28°C
influent	hydantoin	30.9 mg/L
	5-ethyl-5-methylhydantoin	50 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin		
temperature		27°C
influent	5,5-dimethylhydantoin	49.5 mg/L
	5-ethyl-5-methylhydantoin	54 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
trisolute		
temperature		27°C
influent	hydantoin	41.5 mg/L
	5,5-dimethylhydantoin	38 mg/L
	5-ethyl-5-methylhydantoin	33 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
coal gasification wastewater		
temperature		28°C
influent		undiluted
flow rate		100 mL/min
carbon		30.0 g
pH		8.76

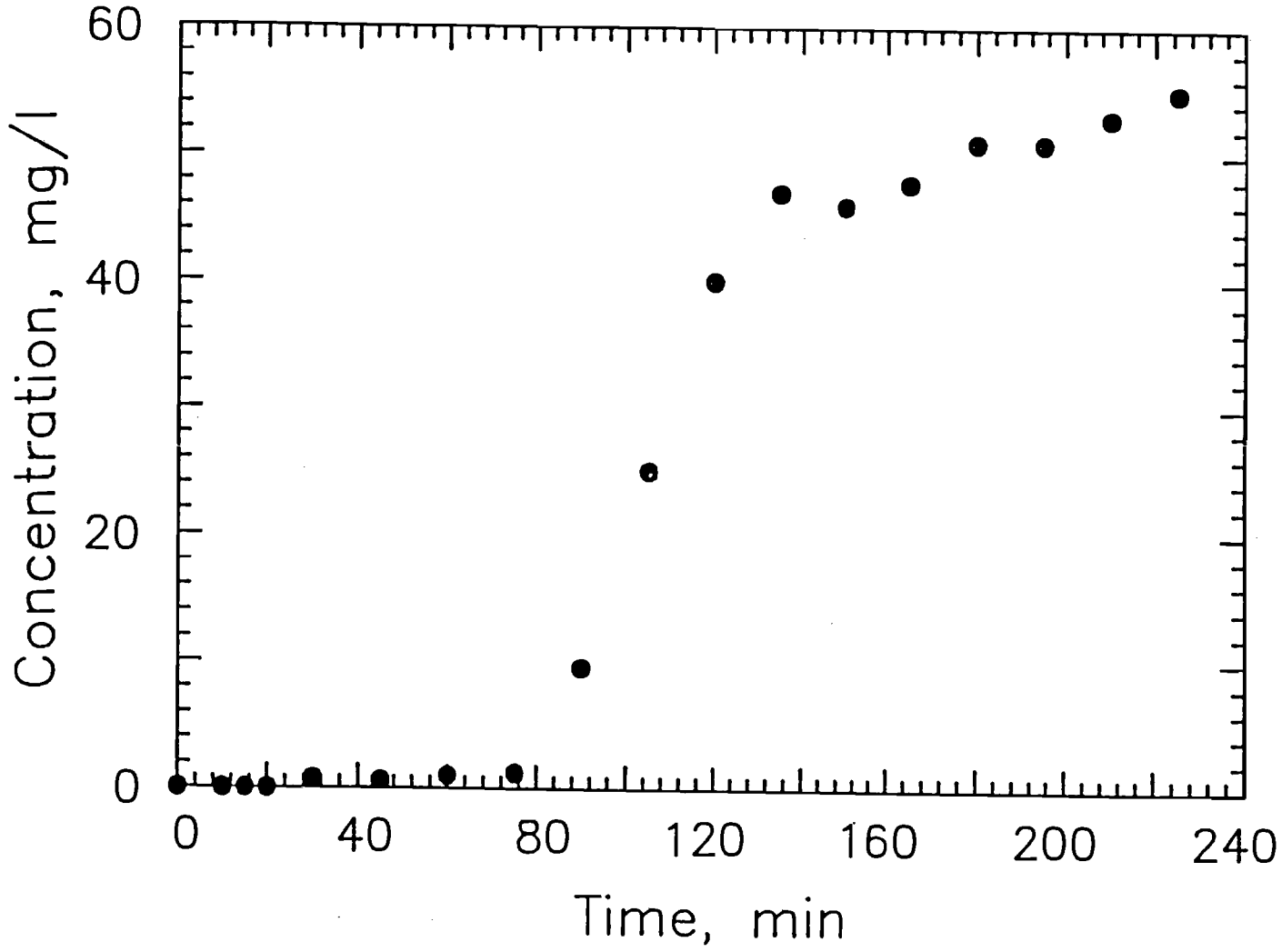

Fig. 45 Column Breakthrough Curve - Hydantoin.

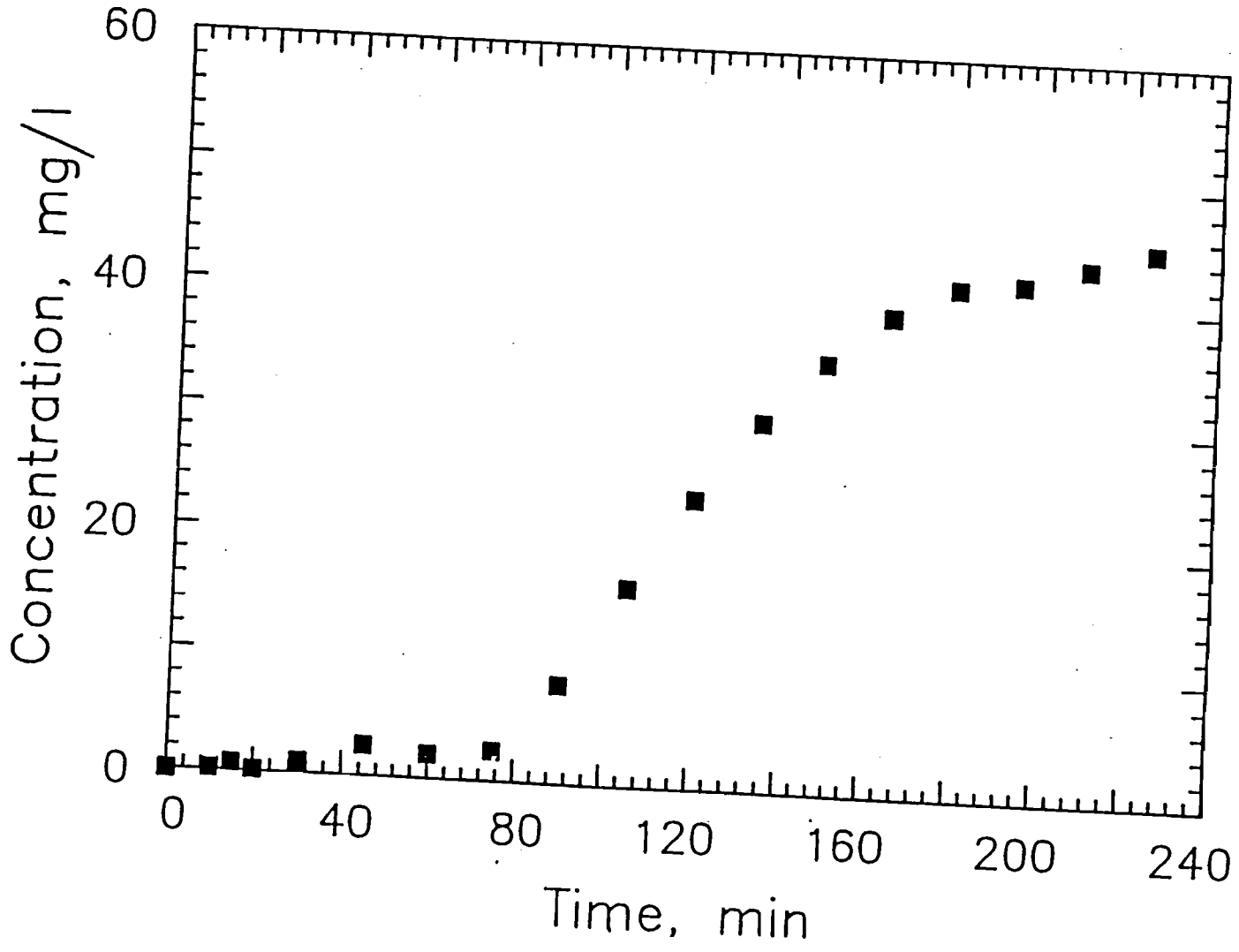

Fig. 46 Column Breakthrough Curve - 5,5-Dimethylhydantoin.

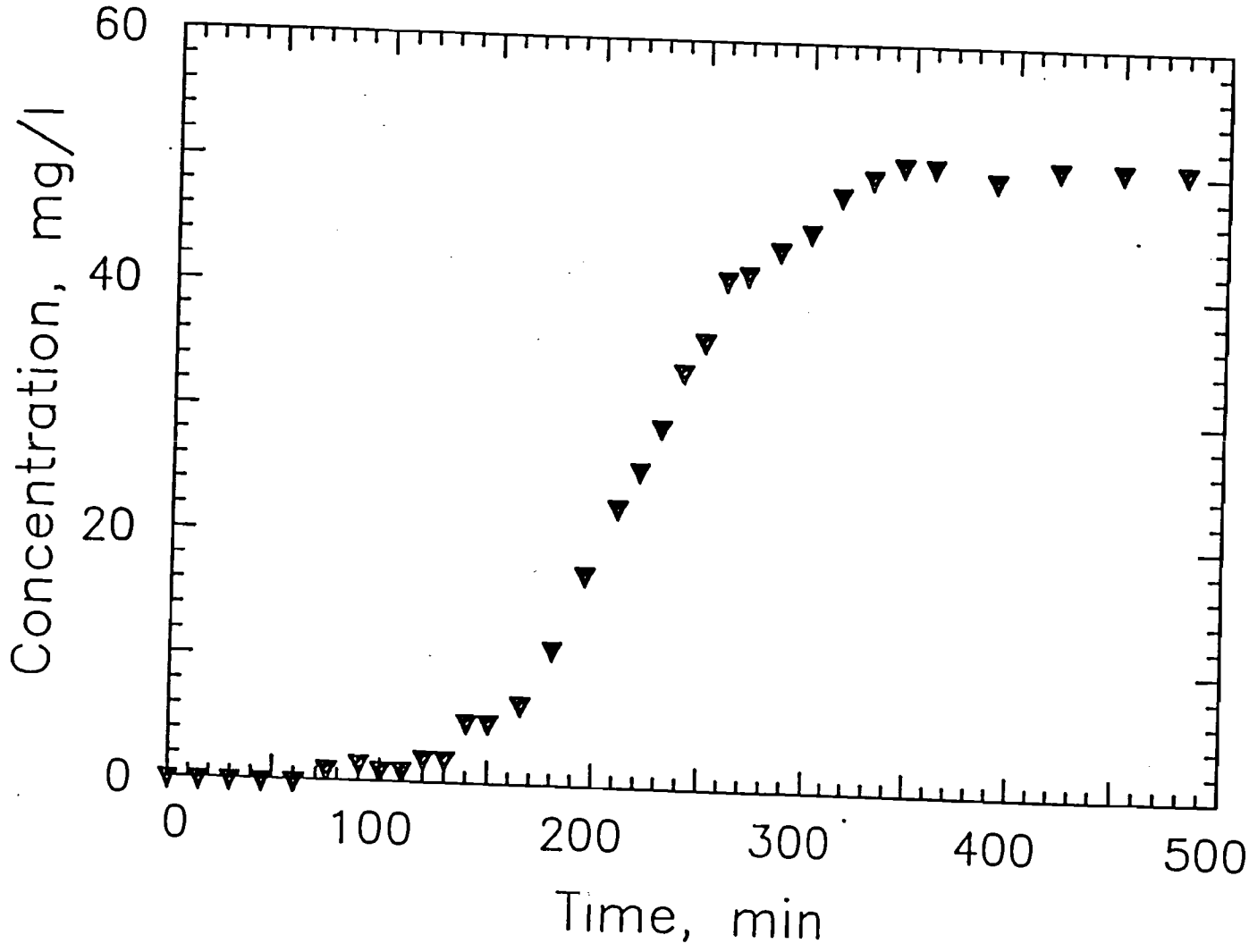

Fig. 47 Column Breakthrough Curve - 5-Methyl-5-Ethylhydantoin.

Table 17. Single Solute Column X/m Values

hydantoin	43.3 mg/g
5,5-dimethylhydantoin	31.1 mg/g
5-ethyl-5-methylhydantoin	61.0 mg/g

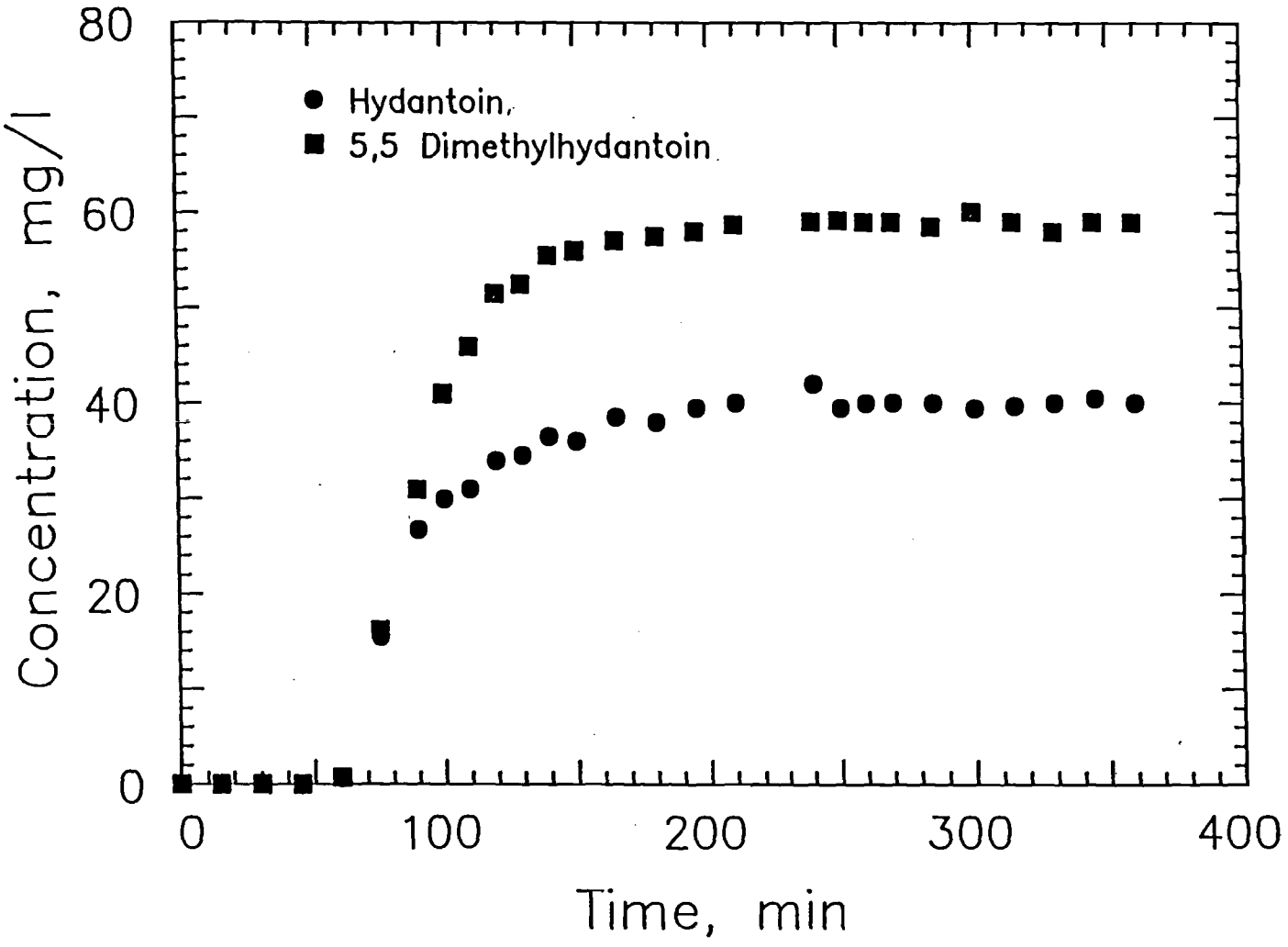

Fig. 48 Bisolute Breakthrough Curve - Hydantoin/5,5-Dimethylhydantoin.

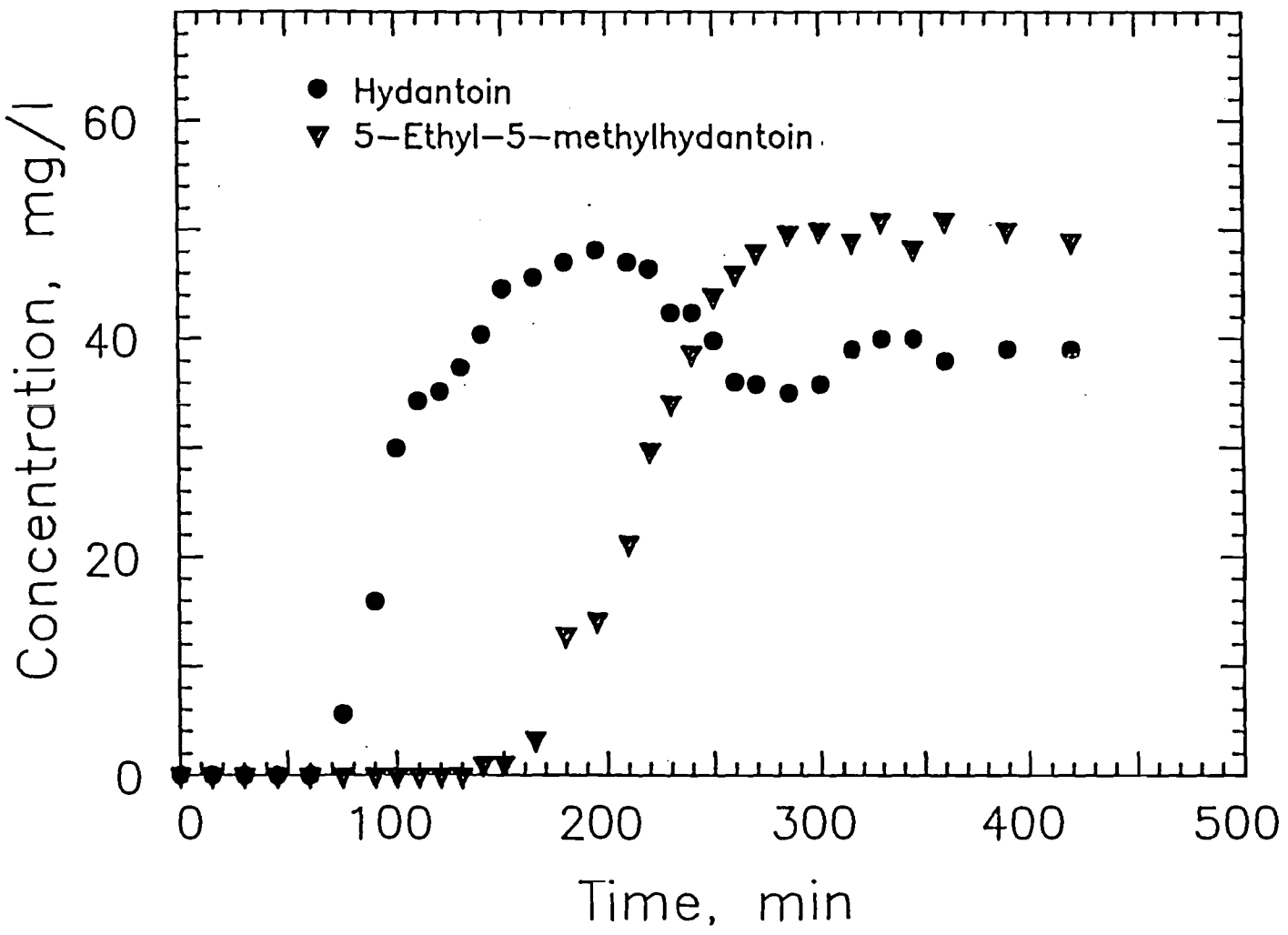

Fig. 49 Bisolute Breakthrough Curve - Hydantoin/5-Methyl-5-Ethylhydantoin.

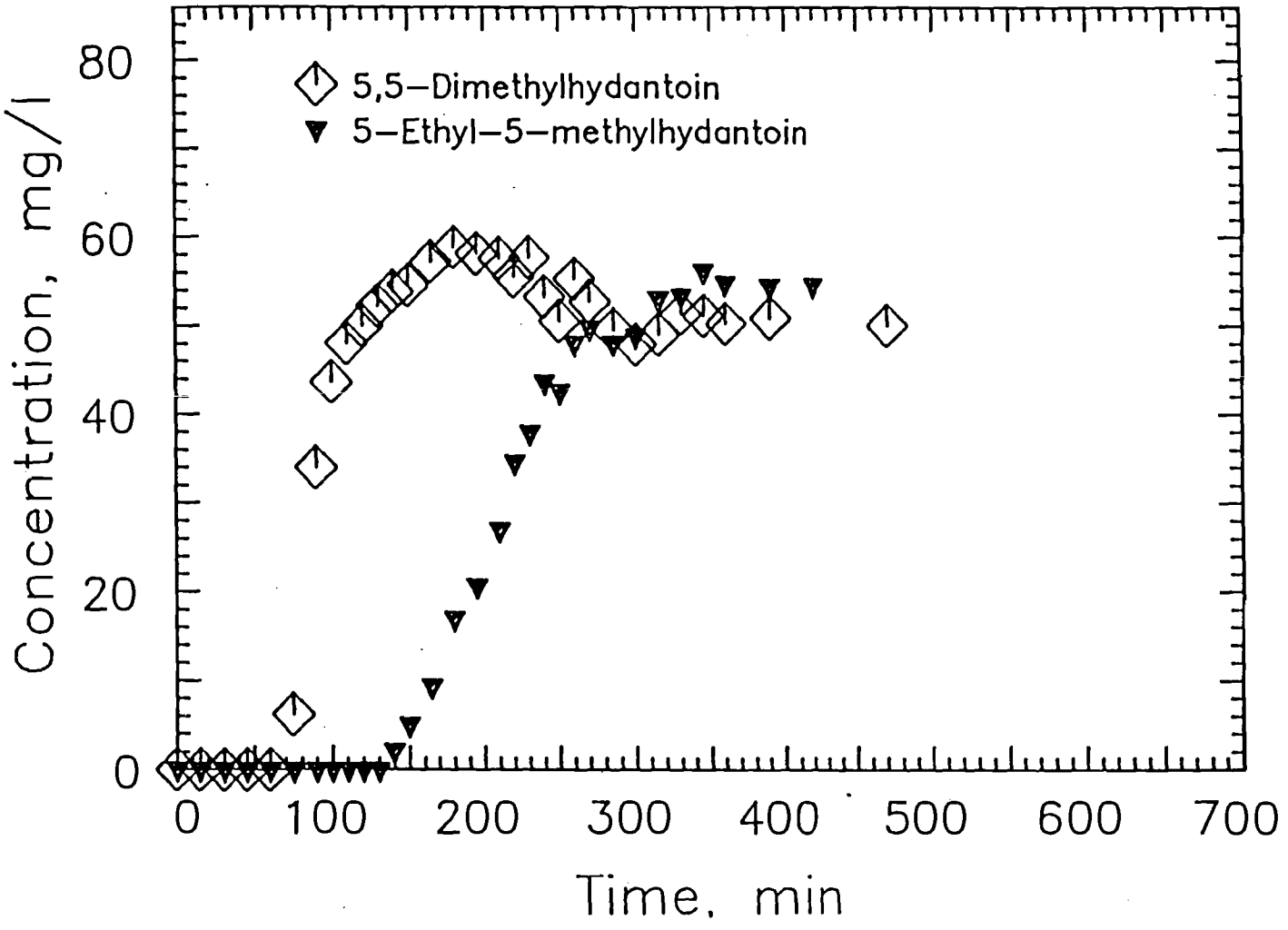

Fig. 50 Bisolute Breakthrough Curve - 5,5-Dimethylhydantoin/5-Methyl-5-Ethylhydantoin.

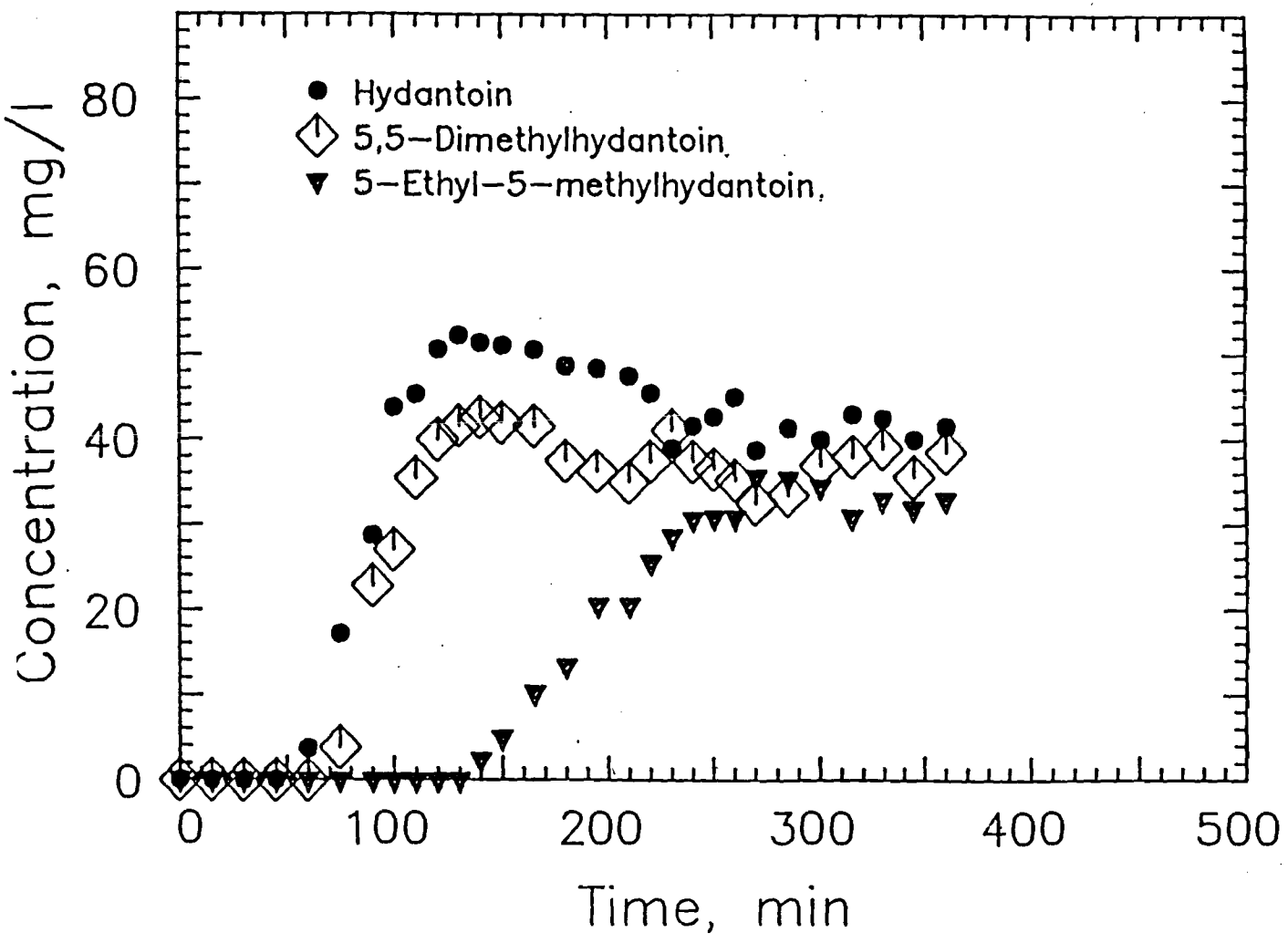

Fig. 51 Trisolute Breakthrough Curve.

Table 18. Bisolute and Trisolute Column X/m Values

hydantoin/5,5-dimethylhydantoin	
hydantoin	21.0 mg/g
5,5-dimethylhydantoin	36.0 mg/g
hydantoin/5-ethyl-5-methylhydantoin	
hydantoin	19.0 mg/g
5-ethyl-5-methylhydantoin	57.0 mg/g
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin	
5,5-dimethylhydantoin	22.0 mg/g
5-ethyl-5-methylhydantoin	58.0 mg/g
trisolute	
hydantoin	17.0 mg/g
5,5-dimethylhydantoin	17.0 mg/g
5-ethyl-5-methylhydantoin	33.0 mg/g

concentration. This was caused by all hydantoin in the influent passing through the column unadsorbed, and additional hydantoin was added to the effluent due to displacement from the carbon through competition with the more strongly adsorbed 5-ethyl-5-methylhydantoin. A comparison of the X/m values in Table 19 also showed that 5-ethyl-5-methylhydantoin was more strongly adsorbed than hydantoin. The bisolute curve 5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin again showed a displacement of the more weakly adsorbed solute, 5,5-dimethylhydantoin, by the more strongly adsorbed 5-ethyl-5-methyl-hydantoin. The X/m value in Table 19 verify that the carbon has a higher adsorption capacity for the 5-ethyl-5-methylhydantoin over the 5,5-dimethyl-hydantoin.

A double displacement effect occurred in the trisolute breakthrough curve. The most strongly adsorbed 5-ethyl-5-methylhydantoin displaced both hydantoin and 5,5-dimethylhydantoin from the carbon as can be see in Figure 51. From Table 18, the X/m values for hydantoin and 5,5-dimethylhydantoin were equal while the carbon exhibited a much higher adsorption capacity for the 5-ethyl-5-methylhydantoin.

Overall, a review of the results in Table 18 show an adsorption preference of 5-ethyl-5-methylhydantoin < 5,5-dimethylhydantoin < hydantoin.

The breakthrough curves for the actual pretreated coal gasification effluent is shown in Figure 52. Immediately following is the breakthrough curve for total organic carbon for the wastewater, Figure 53. The amount of carbon used in the column was 30 grams with a flow rate of 100 mL/min. From Figure 52, the least strongly adsorbed 5,5-dimethylhydantoin broke through first between 10 and 15 minutes from the start of the test followed by 5-ethyl-5-methylhydantoinbreaking through between 15 and 20 minutes. 5,5-Dimethylhydantoin reached carbon exhaustion at 1977 mg/L within 10 minutes of initiating breakthrough. 5-Ethyl-5-methylhydantoin reached influent concentration after 55 minutes. Phenol did not appear until 85 minutes from the test start and slowly reached exhaustion at 165 minutes. A slight displacement of solute occurred with 5,5-dimethylhydantoin being displaced by the 5-ethyl-5-methylhydantoin. Also, slight displacement of the 5-ethyl-5-methylhydantoin by the phenol occurred.

The X/m values for each of the solutes measured in the pretreated coal gasification effluent are shown in Table 19.

At face value, it appears that 5,5-dimethylhydantoin was more strongly adsorbed than phenol in the coal gasification wastewater due to its higher X/m value in Table 19. However, the higher X/m value is due to the concentration of the 5,5-dimethylhydantoin being an order of magnitude higher than the phenol concentration. A more definitive determination of adsorption preferences can be obtained from the coal gasification wastewater breakthrough curves where phenol was the last compound to be observed in the column effluent, and where phenol displaced both 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoinfrom the carbon. Phenol was apparently the most strongly adsorbed compound.

A comparison of the X/m values found in Table 19 with the single solute isotherm curves for 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin (Figures 40 and 41) reveals that the X/m values found in the column study for

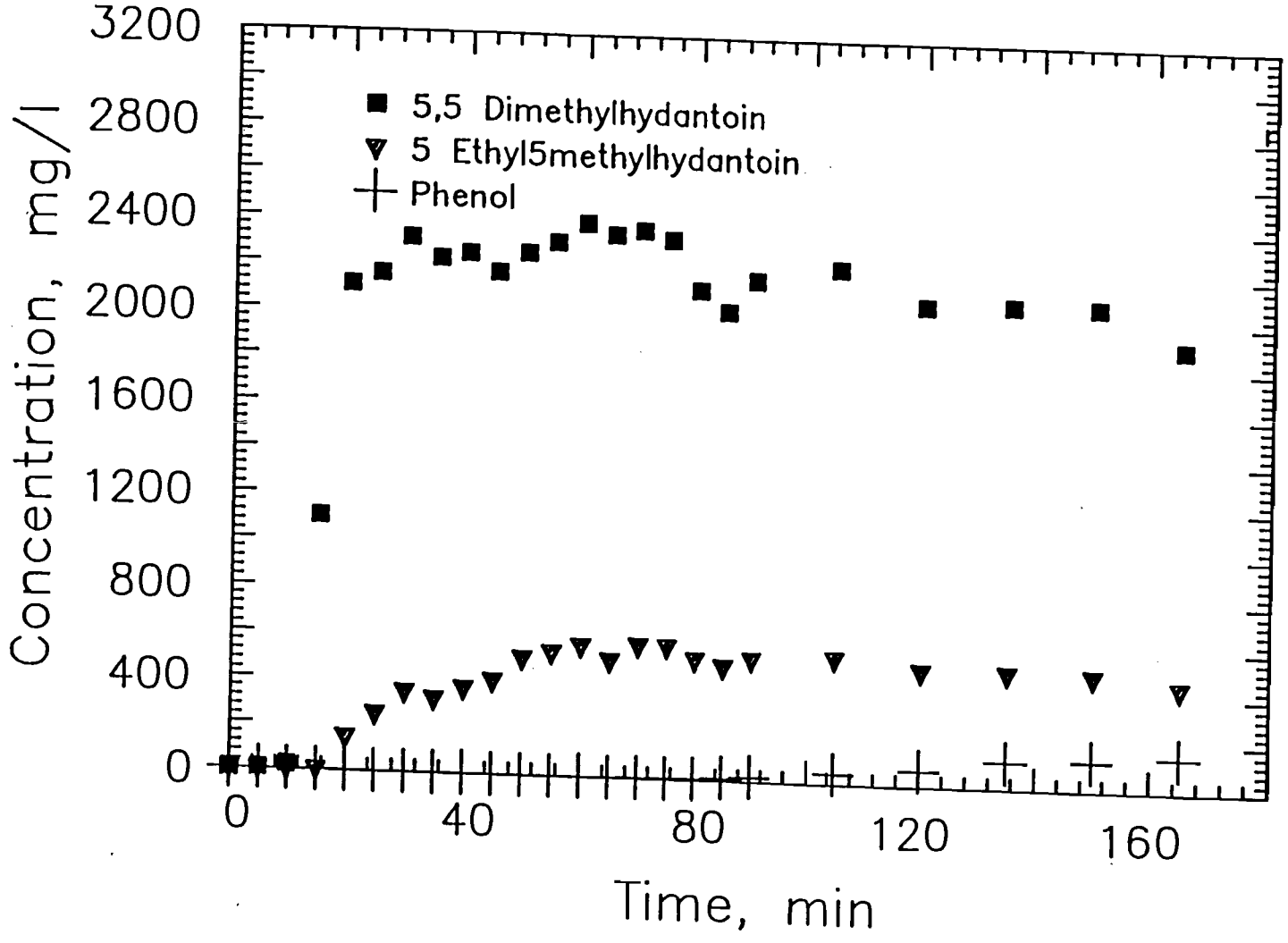

Fig. 52 Breakthrough Curve - Pretreated Coal Gasification Effluent.

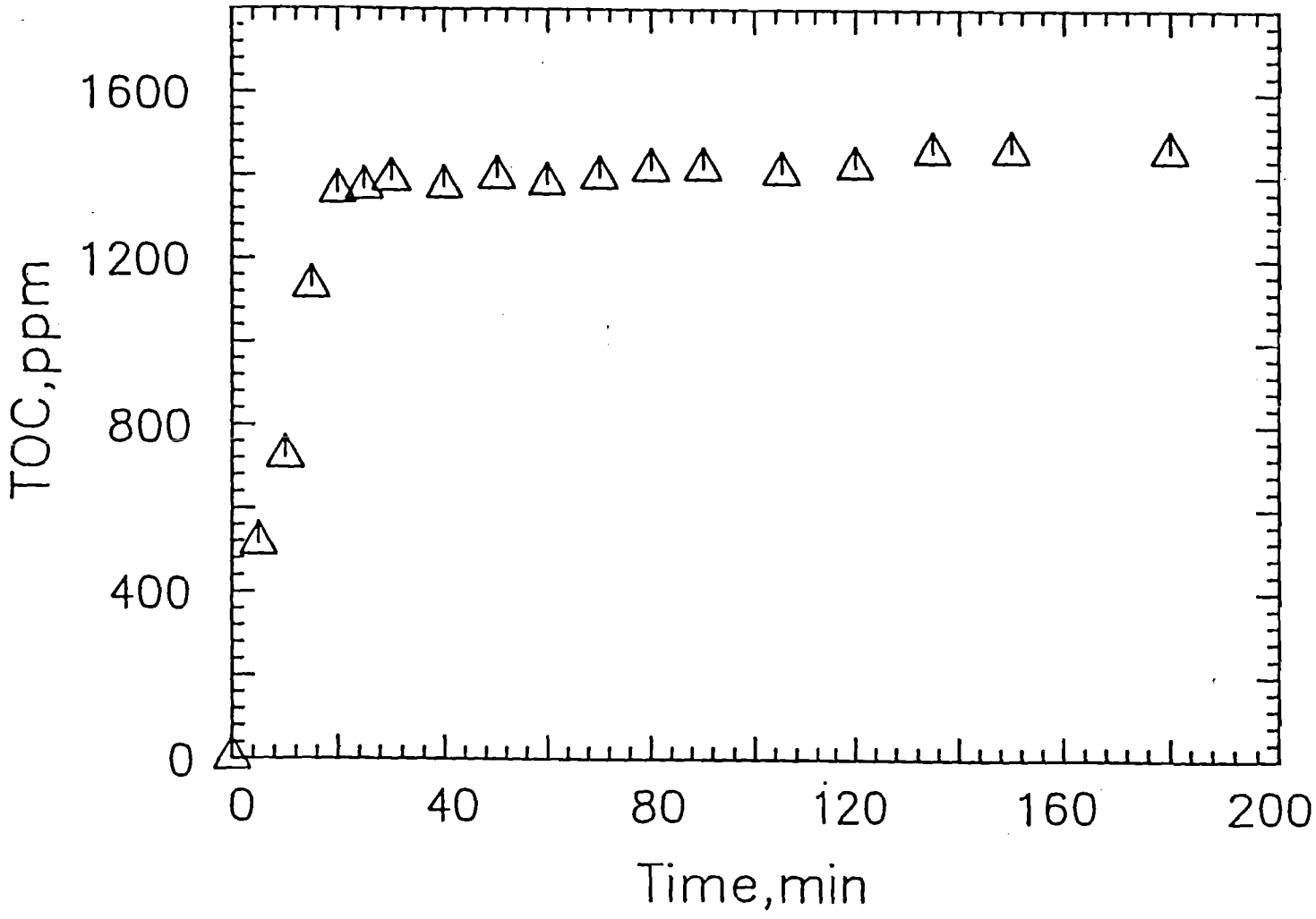

Fig. 53 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent.

Table 19. Pretreated Coal Gasification Effluent X/m Values

5,5-dimethylhydantoin	95.5 mg/g
5-ethyl-5-methylhydantoin	41.8 mg/g
phenol	64.5 mg/g

coal gasification wastewater were significantly lower than the expected X/m values for the pure single solute system given equivalent solute concentrations. A comparison follows in Table 20.

Hydantoin could not be shown since the gas chromatographic columns used retained hydantoin. Other compounds existed in the wastewater which interferenced in using the TOC analyzer to provide an indirect reading of the hydantoin concentration. Therefore, hydantoin concentration could not be determined.

The TOC breakthrough curve is interesting since it shows that the wastewater contains some substances that are apparently not readily adsorbed on activated carbon. This is shown by noting that some TOC broke through the carbon column immediately from the start of the test. It is assumed that the compounds that were not adsorbed were large molecules that could not physically fit inside the carbon pore.

CONCLUSIONS

The batch kinetic tests for single solutes demonstrated that the kinetics of adsorption for hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin were very rapid with most of the adsorption occurring in the first 20 minutes.

The relative strength of adsorption of the three solutes was established by the single solute, bisolute, and trisolute isotherm points as follows: hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin. This relationship held true regardless of the relative concentration of each solute with respect to the other as demonstrated by the coal gasification wastewater breakthrough curve. Even though 5,5-dimethylhydantoin was present in concentrations of 1977 mg/L, 5-ethyl-5-methylhydantoin at concentrations of 456 mg/L was still able to displace it from the carbon, and was therefore more strongly adsorbed. The bisolute and trisolute isotherm points also demonstrated competitive effects between the solutes relative to their respective strengths of adsorption. The X/m values for each adsorbate was markedly reduced by the presence of a second and third solute. Within a given weight of activated carbon, there was a finite number of adsorption sites that could be utilized by the three adsorbates. Although hydantoin was the least strongly adsorbed solute, it was not totally desorbed by either the 5,5-dimethylhydantoin or the 5-ethyl-5-methylhydantoin, and 5,5-dimethylhydantoin was not totally desorbed by the 5-ethyl-5-methylhydantoin. Since the X/m values for the less strongly adsorbed compounds are lower than the corresponding X/m value for the single solute, it is obvious some displacement of the weaker by the more strongly adsorbed compound occurs. However, since an apparently large percentage of the weaker adsorbate, hydantoin, would still be adsorbed on the carbon after the most strongly adsorbed compound, 5-ethyl-5-methylhydantoin, had reached equilibrium, adsorption sites on the carbon appear to have a site specific affinity for one particular solute over the other.

The characteristics of the various adsorbates could be the leading cause of the adsorption preferences encountered. The difference in molecular structure of the three solutes was the presence of the alkyl groups or hydrogen bonded to the C^5. Hydantoin had no alkyl groups and was the most

Table 20. Comparison of X/m Values for Coal Gasification Wastewater and Pure Solutes

5,5-dimethylhydantoin		
	concentration	1977 mg/L
	pure X/m	145 mg/g
	wastewater X/m	95.5 mg/g
5-ethyl-5-methylhydantoin		
	concentration	456 mg/L
	pure X/m	120 mg/g
	wastewater X/m	41.8 mg/g

weakly adsorbed. 5-Ethyl-5-methylhydantoin had the largest molecular weight function groups and was the most strongly adsorbed. 5,5-Dimethylhydantoin was in an intermediate position of adsorption strength. Examples of adsorption strength based upon functional groups attached to the solute molecules were previously found by Belfort (1979).

The pH adjusted isotherm points within the high, mid-range, and low-range for each single solute isotherm conclusively showed that at a pH of 4 and 7, the X/m values were within experimental error of the isotherm curve. At pH 9, however, the X/m value was much lower. Therefore, at a pH of 9, the amount of solute adsorbed per unit weight of carbon is significantly reduced.

The X/m values for the single solute breakthrough curves were either directly on or within experimental error of the X/m value for an equivalent solute concentration on the pure solute breakthrough curves. This phenomena enhances the probability that the single solute isotherms are accurate.

For the bisolute and trisolute curves, the X/m values demonstrated the adsorption preference of the activated carbon for the three adsorbates. From Table 20, it is obvious that 5,5-dimethylhydantoin is more strongly adsorbed than hydantoin from the hydantoin/5,5-dimethylhydantoin X/m values, and from the trisolute X/m values, that 5-ethyl-5-methylhydantoin is more strongly adsorbed than both of the other two adsorbates. Also, by observing the solute displacements which occurred on the actual bisolute and trisolute breakthrough curves (Figures 48 through 51), a relative adsorption preference can be observed.

The pretreated coal gasification effluent breakthrough curves (Figure 52) with its associated X/m values (Table 20) yielded interesting results. A comparison of the X/m values for the coal gasification wastewater and pure solutes for equivalent solute concentrations (Table 20) showed significant reductions in the X/m values in the wastewater. The adsorption of 5,5-dimethylhydantoin was reduced by 34% and that of 5-ethyl-5-methylhydantoin was reduced 65% from the adsorption that would be expected in a pure solute system. The probable reasons for the reduction in adsorption capacity are twofold: (1) the increase in pH from 5.6 in pure systems to 8.76 in the actual wastewater, and (2) competition between the various solutes in the wastewater. From Figures 42, 43, and 44, it was shown that at a pH of 9, the amount of pure solute adsorbed on the carbon was reduced. Since the wastewater has a pH of 8.76, it is probable that the pH had an effect in reducing the X/m values for the waste- water. In addition, from the bisolute and trisolute isotherm points (Figures 42, 43, and 44) it was demonstrated that competition between the solutes will reduce the amount of hydantoins that will be adsorbed on activated carbon. In the coal gasification wastewater, the hydantoins were in competition with phenol (which was more strongly adsorbed) which would reduce the X/m values for the hydantoins. It is probable that both conditions contributed to a reduction in the amount of hydantoins adsorbed.

CARBON REGENERATION STUDY

Continuous flow carbon adsorption - solvent regeneration studies were carried out using 30 x 40 mesh Filtrasorb 400, pretreated (solvent extracted - ammonia stripped) wastewater and a series solvents. Flow rates were 5 mL/min and 2 mL/min for adsorption and regeneration, respectively. The results of the adsorption regeneration cycles are summarized in Table 21. Typical breakthrough and regeneration curves are given in Figures 54, 55, 56, and 57.

CONCLUSIONS

Based on the quantity of carbon required for adsorption and the limited regeneration by the solvents used, it does not appear that this process is a viable one for the removal of hydantoins from the pretreated wastewater.

Table 21. Solvent Regeneration

Solvent	% Capacity Regenerated
NaOH, 0.1 M	70
NaOH, 0.2 M	57,72*
HCl, 0.2 M	38
HCl, 1 M	40
Methanol	69,54,51*
Methyl Ethyl Ketone	48*
2-Propanol	15*

*Successive regeneration cycles.

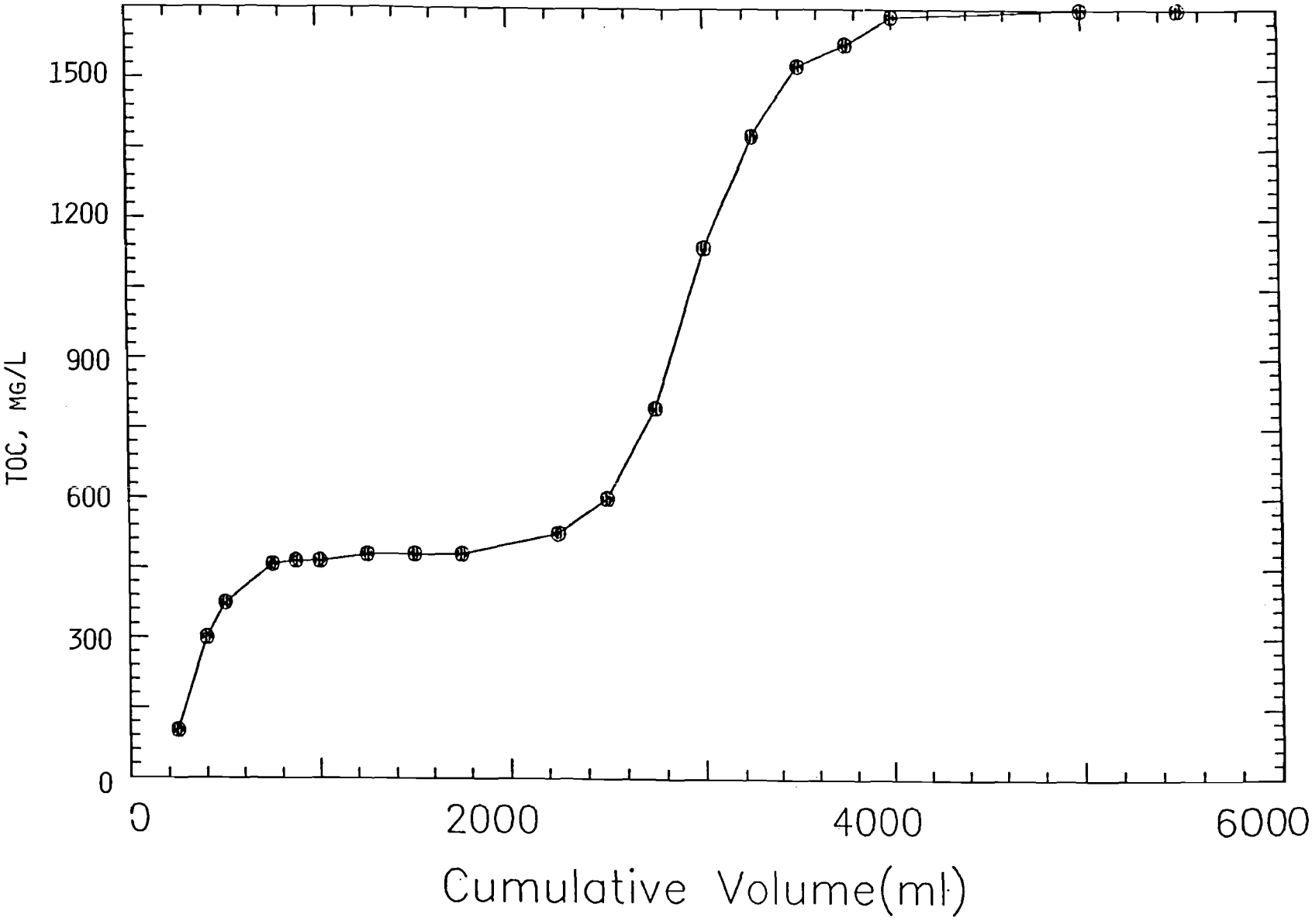

Fig. 54 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent. Adsorption-Regeneration Study

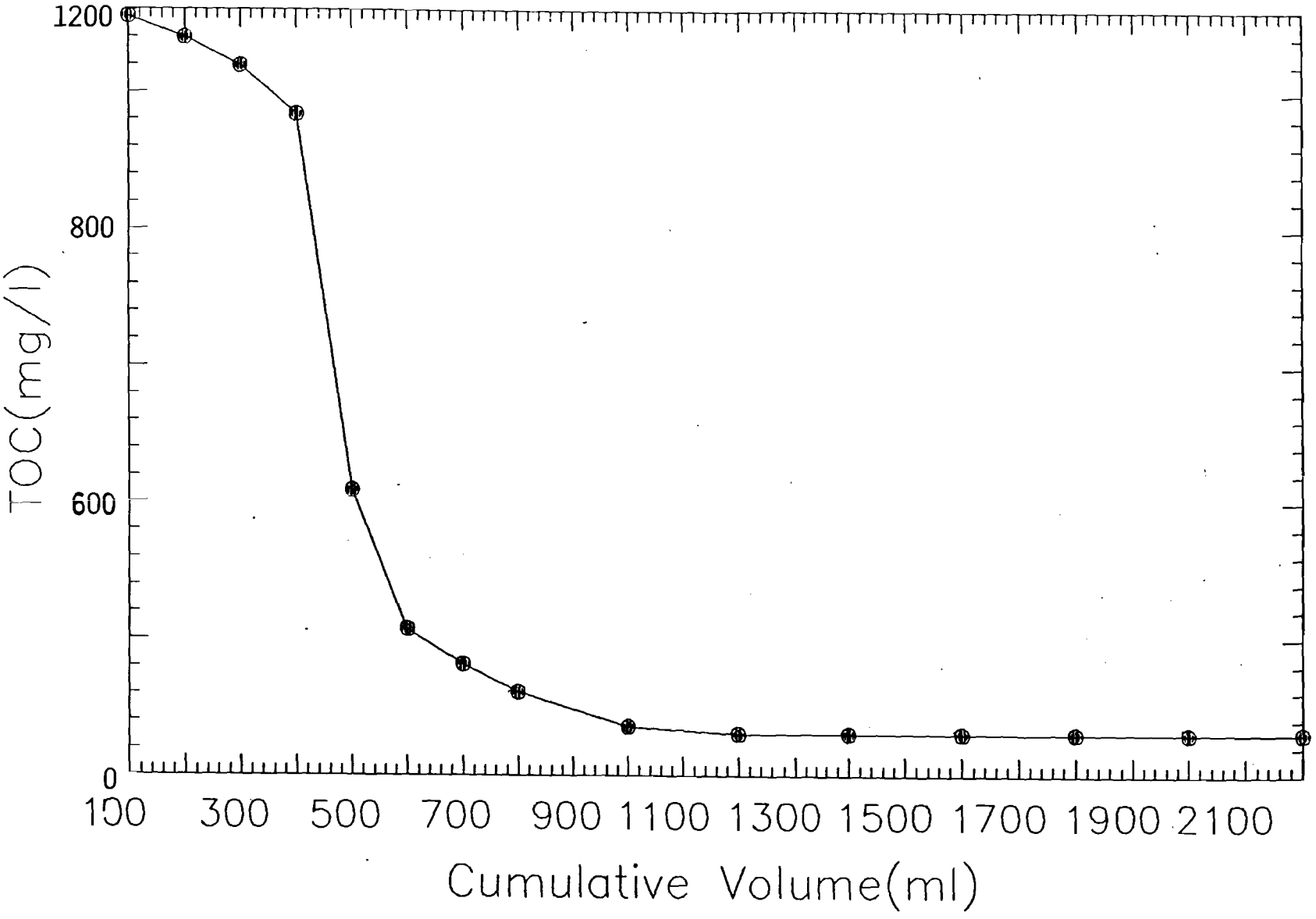

Fig. 55 Solvent Regeneration - Sodium Hydroxide.

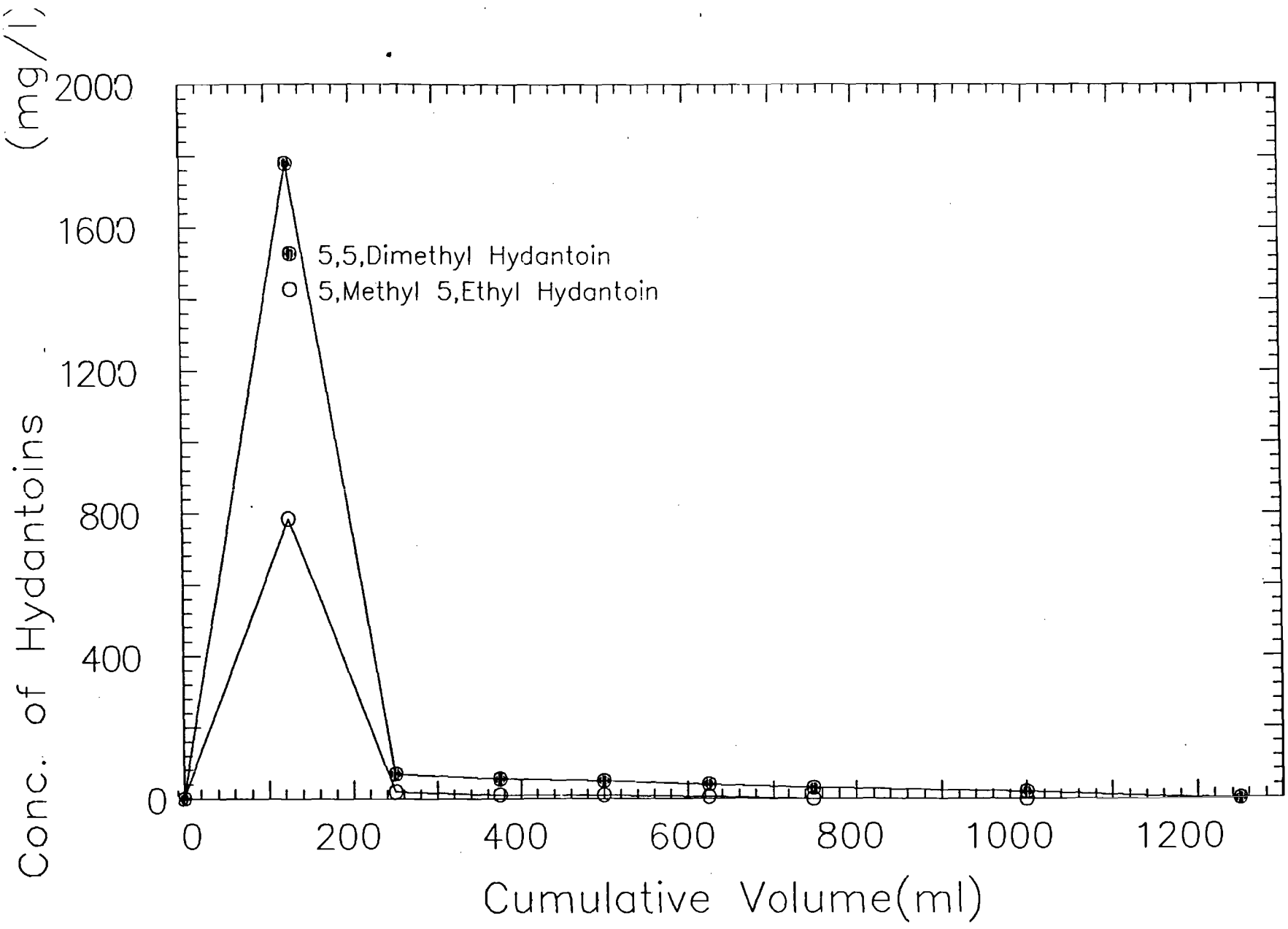

Fig. 56 First Carbon Regeneration - Methanol.

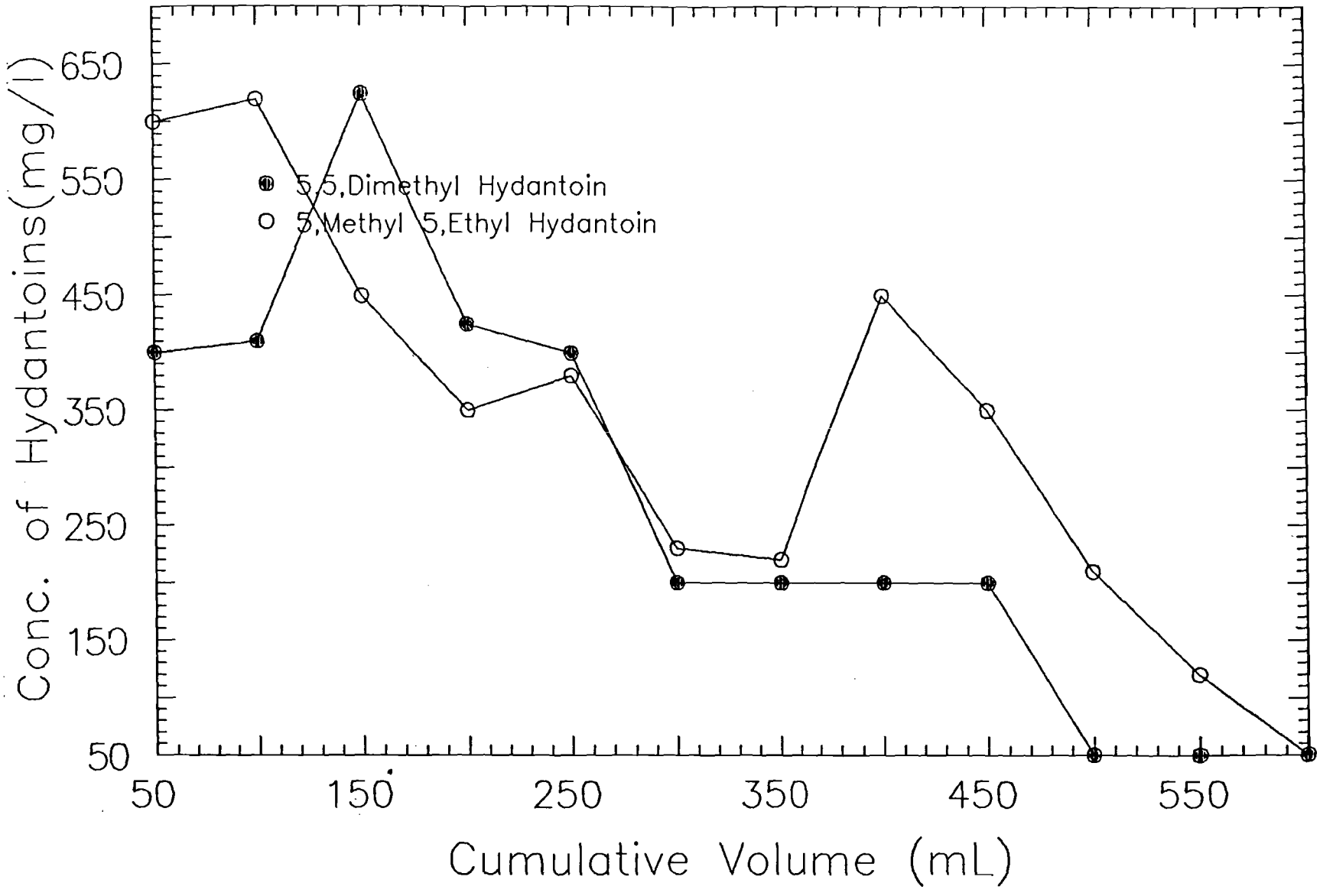

Fig. 57 Second Carbon Regeneration - Methanol.

SUMMARY

Dilute (~10%) coal gasification effluent was successfully treated biologically for the removal of organic carbon and ammonia. The complete treatment train consisted of a two-stage anaerobic removal followed by a single sludge nitrification system for conversion of ammonia nitrogen to nitrate-nitrogen and finally conversion of nitrate-nitrogen to nitrogen gas in a biological denitrification system.

After an extended period of operation on ~10% coal-gasification effluent inhibition of both the anaerobic and the nitrification systems occurred. Inhibition of the anaerobic system was partially overcome by replacement of a portion of the granular activated carbon in the filter. Continued periodic replacement of the activated carbon was required to maintain a viably operating anaerobic filter. Nitrification inhibition was eliminated by either addition of powdered activated carbon to the aeration basin or by the periodic replacement of a portion of the granular activated carbon in the anaerobic filter.

Batch inhibition studies indicated that substituted pyridines (picolines) were inhibitory to the anaerobic system. Inhibition of the nitrification system was attributed to the increase in effluent cresol concentrations from the anaerobic filter as the adsorption capacity of the granular activated carbon was exceeded.

Carbon adsorption-solvent regeneration studies on pure compounds (hydantoin and substituted hydantoins, and on solvent extracted-ammonia stripped coal gasifier effluents indicated that the limited adsorption capacity for the hydantoins coupled with incomplete regeneration of the exhausted carbon would limit the utility of this method as a treatment process for the removal of organic carbon from pretreated coal gasification effluent.

APPENDIX A

Table 1. Characteristics of GFETC Coal Gasification Wastewater

	Concentration[a]
pH	8.2
Total organic carbon (TOC)	11,900
Chemical oxygen demand (COD)	26,900
Total alkalinity (as $CaCO_3$)	25,000
Total suspended solids (TSS)	3,670
Total volatile solids (TVS)	3,180
Total volatile acids (as CH_3COOH)	460
Phenol	5,600
o-Cresol	640
m-Cresol	931
p-Cresol	910
NH_3-N	5,300
CN^-	140
SCN^-	150
S^{-2}	BDL[b]
Metals -	
Chromium	BDL
Zinc	BDL
Nickel	BDL
Copper	BDL
Iron	5.5
Manganese	BDL

[a]mg/L except pH
[b]Below detection limit.

Table 2. Pretreated Wastewater Characteristics[c]

Constituent	Concentration[a]
pH	8.9
TOC	1,700
COD	5,700
Total alkalinity (as $CaCO_3$)	1,500
Methanol	230
Ethanol	BDL[b]
Acetone	10
2-Propanol	BDL
Acetonitrite	2
DIPE	BDL
1-Propanol	BDL
Propionitrite	BDL
Phenol	160
o-Cresol	BDL
m-Cresol	BDL
p-Cresol	BDL
5,5-Dimethylhydantoin	2,140
5-Methyl-5-ethylhydantoin	490
Total volatile acids (as CH_3COOH)	BDL
NH_3	560
Sulfide	8
Cyanide	39
Thiocyanate	210

[a]mg/L
[b]Below Detection Limit
[c]Solvent Extracted-Ammonia Stripped

QUANTITATION REPORT (TYPE: CGW)

DATA: CGW721.TI
10/29/81 13:26:00
SAMPLE: COAL GASIFICATION WASTEWATER V.P.E.(7 TS
CONDS.: SE54 30M,*84,40(3)300 4/M,SPLITLESS II
FORMULA: - INSTRUMENT: FINN I: 0
SUBMITTED BY: MFG ANALYST: MFG. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

Table 3. Minor Constituents of GFETC Gasification Effluent.

NO	NAME	SCAN	FIT	PURITY	LIBRARY ENTRY	AREA	AMOUNT	%TOT
1	BENZOFURAN,2,3-DIHYDRO-	1207	976	836	NB 2474	69615.	45.917	5.79
2	PHENOL,4-(1-METHYLETHYL)-	1231	956	820	NB 861	39128.	25.808	3.26
3	PHENOL,2-ETHYL-5-METHYL-	1243	960	871	NB 5449	122386.	80.725	10.19
4	UNKNOWN	1246	940	660	NB 6076			
5	5-ISOBENZOFURANCARBOXYLICACID,1,3-DIHYDRO-1,3-DIOXO-	1258	675	511	NB 2839	1599.	1.055	0.13
6	PHENOL,4-ETHYL-2-METHYL-	1281	938	802	NB 6076	151610.	100.000	12.62
7	PHENOL,2,3,5-TRIMETHYL-	1295	866	665	NB 3908	53783.	35.474	4.48
8	ETHANONE,1-(2,4-DIHYDROXYPHENYL)-	1300	988	747	NB 583	35886.	23.670	2.99
9	1H-INDOLE	1320	998	829	NB 1488	45739.	30.169	3.81
10	DECANE,3-BROMO-	1326	759	523	NB 16274	9907.	6.534	0.82
11	PROPANOICACID,2,2-DIMETHYL-,2-(1,1-DIMETHYLETHYL)PHENYLESTER	1331	666	368	NB 20924	4820.	3.179	0.40
12	NONANOICACID	1334	984	702	NB 1362	18618.	12.280	1.55
13	PHENOL,2,3,5-TRIMETHYL-	1337	987	784	NB 3908	14127.	9.318	1.18
14	BENZENEMETHANOL,AR-ETHENYL-	1343	795	660	NB 16282	1806.	1.244	0.16
15	1,3-BENZENEDIOL,4,5-DIMETHYL-	1351	881	568	NB 2678	7871.	5.192	0.66
16	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1355	953	506	NB 15415	11847.	7.814	0.99
17	BENZENEMETHANOL,AR-ETHENYL-	1362	969	761	NB 16282	42614.	28.108	3.55
18	2H-1-BENZOPYRAN-2-ONE,3,4-DIHYDRO-	1370	769	530	NB 1470	2298.	1.516	0.19
19	UNKNOWN	1374	698	467	ND 2974			
20	PHENOL,2-(1-METHYLPROPYL)-	1378	758	660	NB 575	2449.	1.616	0.20
21	2-PROPENAL,3-PHENYL-	1384	980	818	NB 1006	14596.	9.627	1.21
22	BENZOFURAN,7-METHYL-	1388	981	874	NB 11795	14629.	9.649	1.22
23	BENZENE,1-ETHYL-2,4,5-TRIMETHYL-	1400	880	706	NB 12129	95745.	63.152	7.97
24	UNKNOWN	1404	826	431	NB 6740			
25	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1417	989	824	NB 15415	34774.	22.936	2.89
26	UNKNOWN	1420	780	466	NB 17899			
27	2-PROPENAL,3-PHENYL-	1421	978	704	NB 1006	37618.	24.812	3.13
28	2-PROPENAL,3-PHENYL-	1422	981	754	NB 1006	37783.	24.921	3.14
29	BENZENEPROPANOL,2-HYDROXY-	1430	728	405	NB 5168	5083.	3.300	0.42
30	BENZENEMETHANOL,.ALPHA.-ETHYL-4-METHOXY-	1438	822	571	NB 8409	9519.	6.279	0.79
31	1,9-NONANEDIOL,DIMETHANESULFONATE	1451	726	397	NB 7695	2460.	1.622	0.20
32	DECANOICACID	1462	881	680	NB 2029	6500.	4.287	0.54
33	1-NAPHTHALENOL,1,2,3,4-TETRAHYDRO-	1466	769	519	NB 2692	11564.	7.627	0.96
34	1H-INDOLE,3-METHYL-	1467	974	598	NB 490	9363.	6.176	0.78
35	BENZENE,\2-(METHYLSULFINYL)ETHENYL\-	1472	721	436	NB 9726	13146.	8.671	1.09
36	2-PROPYN-1-OL,3-P-TOLYL-	1485	697	357	NB 11341	3298.	2.176	0.27
37	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1504	979	792	NB 15415	10401.	6.860	0.87
38	BENZENE,1,3-DIMETHYL-5-(1-METHYLETHYL)-	1512	887	423	NB 8007	4375.	2.686	0.36
39	BENZENE,2,4-DIMETHYL-1-(1-METHYLETHYL)-	1517	777	580	NB 8006	5094.	3.360	0.42
40	BENZENE,(1,1-DIMETHYLETHYL)METHYL-	1531	804	471	NB 15328	1807.	1.192	0.15
41	BENZENE,HEXAMETHYL-	1538	767	554	NB 549	14698.	9.695	1.22
42	1H-INDENE-1,2-DIOL,2,3-DIHYDRO-1-METHYL-,CIS-	1539	815	450	NB 24305	10990.	7.249	0.91
43	2-PROPYN-1-OL,3-P-TOLYL-	1549	834	663	NB 11341	5381.	3.549	0.45
44	BIPHENYLENE	1553	978	937	NB 1880	9014.	5.945	0.75
45	BENZENE,HEXAMETHYL-	1563	992	854	NB 549	66497.	43.861	5.53
46	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1577	959	771	NB 9337	9584.	6.322	0.80
47	2-PROPYN-1-OL,3-P-TOLYL-	1583	900	657	NB 11341	14062.	9.275	1.17
48	BENZENE,HEXAMETHYL-	1584	600	558	NB 549	9002.	5.938	0.75
49	ACENAPHTHYLENE,1,2-DIHYDRO-	1610	951	800	NB 488	3169.	2.090	0.26
50	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1628	890	572	NB 9337	2266.	1.494	0.19
51	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1644	833	635	NB 9337	2905.	1.916	0.24
52	2-NAPHTHALENOL	1662	992	690	NB 1678	17945.	11.836	1.49
53	2-NAPHTHALENOL	1675	980	834	NB 1670	21025.	13.868	1.75
54	1-NAPHTHALENOL,3-METHYL-	1739	928	802	NB 10488	1796.	1.185	0.15
55	1H-PHENALENE	1764	939	823	NB 1836	5589.	3.687	0.47
56	1-NAPHTHALENOL,3-METHYL-	1822	973	889	NB 10480	7255.	4.785	0.60
57	1-NAPHTHALENOL,3-METHYL-	1837	829	749	NB 10488	4479.	2.955	0.37
58	DIBENZOFURAN,4-METHYL-	1850	893	708	NB 9509	1063.	0.701	0.09
59	1H-PYRAZOLE,3-METHYL-5-PHENYL-	1868	732	614	NB 7024	2009.	1.325	0.17
60	PHENANTHRENE	2067	967	927	NB 518	5442.	3.589	0.45
61	PHOSPHINE,BIS(PENTAFLUOROPHENYL)PHENYL-	2209	845	785	NB 8245	1766.	1.165	0.15
62	BENZENETETRACARBOXYLLICACID TETRAMETHYLESTER	2643	822	744	NB 25414	31691.	20.903	2.64

Table 3. Minor Constituents of GFETC Gasification Effluent.

SAMPLE: COAL GASIFICATION [illegible]
CONDS.: SE54 30M,*84,40(3)300 4/M,SPLITLESSINCL
FORMULA: PH12 INSTRUMENT: FINN WT: 0.0
SUBMITTED BY: MFG ANALYST: MFG. ACCT. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

NO	NAME	SCAN	FIT	PURITY	LIBRARY	ENTRY	AREA	AMOUNT	%TOT
1	ACETAMIDE,2,2,2-TRIFLUORO-N-METHYL-	1078	783	489	NB	4125	10232.	4.490	0.82
2	1H-1,2,3-TRIAZOLE-4-CARBOXYLICACID,4,5-DIHYDRO-1-PHENYL-	1085	765	615	NB	21120	7747.	3.480	0.62
3	5(4H)-INDANONE,TETRAHYDRO-,TRANS-	1097	696	519	NB	7985	11346.	4.979	0.91
4	AZETIDINE,2-PHENYL-	1100	577	341	NB	13929	738.	0.324	0.06
5	1H-IMIDAZOLE,2-ETHYL-	1114	763	514	NB	4676	11086.	4.865	0.89
6	3-PENTEN-2-ONE,3-ETHYL-4-METHYL-	1121	920	737	NB	13789	9249.	4.059	0.75
7	PHENOL,2,4-DIMETHYL-	1131	873	734	NB	1845	5083.	2.231	0.41
8	CYCLOPENTANE,NITRO-	1137	880	538	NB	6465	1705.	0.748	0.14
9	4-PENTEN-1-OL	1141	731	368	NB	4151	3968.	1.741	0.32
10	BORANAMINE,N,N,1-TRIMETHYL-1-PHENYL-	1153	733	668	NB	7186	2613.	1.147	0.21
11	PHENOL,3-ETHYL-	1159	983	983	NB	3417	61273.	26.891	4.94
12	UNKNOWN	1162	978	882	NB	3417			
13	CYCLOHEXENE,1-METHYL-4-(1-METHYLETHYL)-,(+)-	1180	751	564	NB	4952	2022.	0.888	0.16
14	PHENOL,2,5-DIMETHYL-	1194	980	880	NB	735	53967.	23.684	4.35
15	PHENOL,3,4-DIMETHYL-	1198	996	980	NB	726	59471.	26.100	4.79
16	CYCLOHEXANE,1,1'-(OXYDI-2,1-ETHANEDIYL)BIS-4-METHYL-	1209	794	345	NB	21684	1084.	0.476	0.09
17	BENZOFURAN,2,3-DIHYDRO-	1223	975	830	NB	2474	51433.	22.572	4.15
18	PHENOL,4-METHOXY-	1237	963	725	NB	1780	2906.	1.275	0.23
19	ISOQUINOLINE	1254	998	940	NB	1467	105388.	46.251	8.50
20	QUINOLINE	1259	983	915	NB	623	32501.	14.263	2.62
21	NICOTINONITRILE,1,4-DINYDRO-1-METHYL-4-OXO-	1279	932	658	NB	4052	9239.	4.055	0.74
22	ISOQUINOLINE	1292	989	894	NB	1467	20674.	9.073	1.67
23	1,3-CYCLOHEXADIENE,1,2,6,6-TETRAMETHYL-	1299	755	488	NB	2614	2772.	1.216	0.22
24	BENZENE,(3-METHOXY-1-PROPENYL)-	1300	789	387	NB	11453	2415.	1.060	0.19
25	1H-INDEN-1-ONE,2,3-DIHYDRO-	1314	933	820	NB	489	1643.	0.721	0.13
26	2-PROPENENITRILE	1328	975	545	NB	1111	5888.	2.584	0.47
27	UNKNOWN	1335	992	744	NB	1488			
28	1H-INDOLE	1338	984	932	NB	1488	18627.	8.175	1.50
29	1,3-BENZENEDIOL,4-ETHYL-	1344	816	368	NB	6734	2408.	1.853	0.19
30	1,3-BENZENEDIOL,4,5-DIMETHYL-	1353	820	704	NB	2678	2375.	1.842	0.19
31	ISOQUINOLINE,3-METHYL-	1370	946	848	NB	4820	19221.	8.435	1.55
32	BENZENEMETHANOL,AR-ETHENYL-	1376	970	744	NB	16282	29177.	12.805	2.35
33	2,5-CYCLOHEXADIENE-1,4-DIONE,2,3,5,6-TETRAMETHYL-	1384	892	852	NB	2675	6041.	2.651	0.49
34	UNKNOWN	1386	842	550	NB	2675			
35	BENZENEETHANOL,3-HYDROXY-	1391	759	588	NB	10375	7357.	3.229	0.59
36	FORMAMIDE,N-PHENYL-	1394	874	788	NB	977	8970.	3.937	0.72
37	2-PROPENAL,3-PHENYL-	1401	983	792	NB	1886	29286.	12.853	2.36
38	BENZENEMETHANOL,AR-ETHENYL-	1413	959	888	NB	16282	82798.	36.338	6.67
39	BENZOFURAN,7-METHYL-	1422	947	548	NB	11795	11420.	5.012	0.92
40	BENZOFURAN,7-METHYL-	1437	977	697	NB	11795	24237.	10.637	1.95
41	QUINOLINE,3-METHYL-	1444	930	831	NB	3331	2664.	1.169	0.21
42	QUINOLINE,5-METHYL-	1463	879	553	NB	9695	1890.	0.470	0.09
43	QUINOLINE,4-METHYL-	1471	968	865	NB	2446	3836.	1.333	0.24
44	BENZENECARBOXIMIDOYLBROMIDE,N-METHYL-	1489	876	616	NB	19882	8458.	3.712	0.68
45	ETHANONE,1-PHENYL-,OXIME	1516	872	668	NB	3346	227859.	100.000	18.37
46	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1525	933	807	NB	15415	9664.	4.241	0.78
47	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1540	992	822	NB	15415	7197.	3.159	0.58
48	1,4-BENZENEDICARBOXALDEHYDE,2-METHYL-	1547	925	776	NB	15415	2366.	1.038	0.19
49	2-PROPYN-1-OL,3-P-TOLYL-	1563	917	746	NB	11341	5083.	2.231	0.41
50	NAPHTHALENE,1,2,3,4-TETRAHYDRO-1-METHYL-	1569	830	694	NB	5249	8601.	3.810	0.70
51	BENZENE,HEXAMETHYL-	1585	992	881	NB	549	89901.	39.455	7.25
52	1H-PYRROLO-2,3-B-PYRIDINE	1597	912	542	NB	1889	6863.	3.012	0.55
53	2-PROPYN-1-OL,3-P-TOLYL-	1604	927	717	NB	11341	16915.	7.423	1.36
54	AZETIDINE,2-PHENYL-	1632	835	703	NB	13929	22633.	9.933	1.82
55	ETHANOL,2-(1-PHENYLHYDRAZINO)-	1639	816	617	NB	19496	4489.	1.970	0.36
56	BENZENEETHANAMINE,N-(PHENYLMETHYLENE)-	1648	713	564	NB	6950	33343.	14.633	2.69
57	2-PENTEN-1-ONE,1-(2-HYDROXY-5-METHYLPHENYL)-	1667	668	411	NB	19996	2121.	0.931	0.17
58	TEREPHTHALALDEHYDE,2,5-DIMETHYL-	1683	891	735	NB	9337	1135.	0.498	0.09
59	2-NAPHTHALENOL	1696	988	889	NB	1678	19380.	8.505	1.56
60	BENZO-B-THIOPHENE,2,7-DIMETHYL-	1716	732	489	NB	11555	859.	0.377	0.07
61	BENZENEETHANAMINE,N-(PHENYLMETHYLENE)-	1723	777	466	NB	6950	894.	0.393	0.07
62	1H-BENZIMIDAZOLE-2-CARBOXALDEHYDE	1772	630	482	NB	7000	2061.	0.904	0.17
63	ETHANONE,1-PHENYL-,OXIME	1777	829	513	NB	3346	3041.	1.334	0.25
64	1-NAPHTHALENOL,3-METHYL-	1851	959	833	NB	10488	3495.	1.534	0.28
65	1-NAPHTHALENOL,3-METHYL-	1861	918	704	NB	10488	2653.	1.164	0.21
66	1,4-NAPHTHALENEDIONE,2,3-DIMETHYL-	1877	933	881	NB	6835	1859.	0.465	0.09
67	1-NAPHTHALENOL,3-METHYL-	1893	890	707	NB	10488	2677.	1.175	0.22
68	ISOQUINOLINE,1-ETHYL-	2077	749	482	NB	9699	2909.	1.277	0.23
69	BENZENETETRACARBOXYLLICACID TETRAMETHYLESTER	2671	824	746	NB	25414	29788.	13.838	2.39

APPENDIX B

TREATMENT SYSTEMS

Two-Stage Anaerobic Reactor System

The two-stage pilot-scale anaerobic filter columns employed in this study (Figure 58) consist of two identical Plexiglas columns, each having a height of 183 cm and an internal diameter of 10 cm. Each of these columns was connected to a 20-cm-long inverted conical base to accommodate the influent. The upper end of the first-stage column was connected to a similar conical effluent section also equipped to allow gas collection while the second-stage column was connected to a 30-cm-long by 15-cm-i.d. expansion chamber to allow for the settling of gas-bound carbon particles. A 13-cm-diam concentric Plexiglas water jacket was placed around each column to maintain constant temperature conditions (35 ± 0.5°C). The water jackets were connected, in series, to a constant temperature water bath (Lauda model B, Westbury, NY).

The first-stage filter was packed with Raschig rings (0.5-in. nominal size) to a depth of 173 cm, whereas the second-stage fluidized bed column was packed to a depth of 125 cm with 10 x 20 U.S. mesh Filtrasorb 400 granular activated carbon (Calgon Corp., Pittsburgh, PA). A ½-hp stainless-steel centrifugal pump (Teel Pump, Dayton, OH) was used for recirculation and to fluidize the granular activated carbon to minimize gas entrainment, to provide dilution, and to furnish buffering capacity.

Anaerobic Columns in Series

The anaerobic activated carbon columns in series were of identical size and design of those used in the two-stage anaerobic reactor system and are depicted in Figure 59.

Nitrification Reactor

The biological nitrification system used in this study (Figure 60) was a single-stage, completely mixed activated sludge unit which consisted of an aeration basin (18.5-cm internal diameter, 40-cm height, 10.8-L volume) was fed with a variable flow positive displacement pump. Compressed air was controlled by a pressure regulator, metered with a rotameter, and supplied from a diffuser at the bottom of the basin. The clarifier consisted of a plexiglas column (10-cm internal diameter by 80-cm height, 6.6-L volume) with an inverted conical base and a rotating sludge scraper to minimize sludge adhering to the wall of the clarifier or clogging the conical bottom. A tubing pump was used for sludge recycle to the aeration basin. Both the tubing pump and scraper were operated intermittently by a timer. The system was operated indoors at ambient temperature (19 to 23°C) for 1 year.

Denitrification Reactor

Suspended growth denitrification of anaerobically treated and nitrified wastewater with cell recycle was performed in a 10-L covered reactor. The reactor was coupled to a small aeration basin which was used to remove nitrogen gas prior to clarification, as presented in Figure 61. Settled solids were recycled to maintain the proper solids retention time. Influent (nitrification effluent and methanol solution) was applied to the denitrification reactor from two reservoirs equipped with variable-speed, positive-displacement pumps (Fluid Metering, Inc., Oyster Bay, NY). An airtight cylindrical acrylic reactor served as the denitrification chamber (dimensions are given in Table 22). The reactor was equipped with a variable speed stirrer, which was continuously operated at 2500-3000 rpm. Nitrogen gas was supplied at a rate of 80-109 mL/min to strip oxygen from the influent and to exclude air from the reactor. The effluent from the denitrification

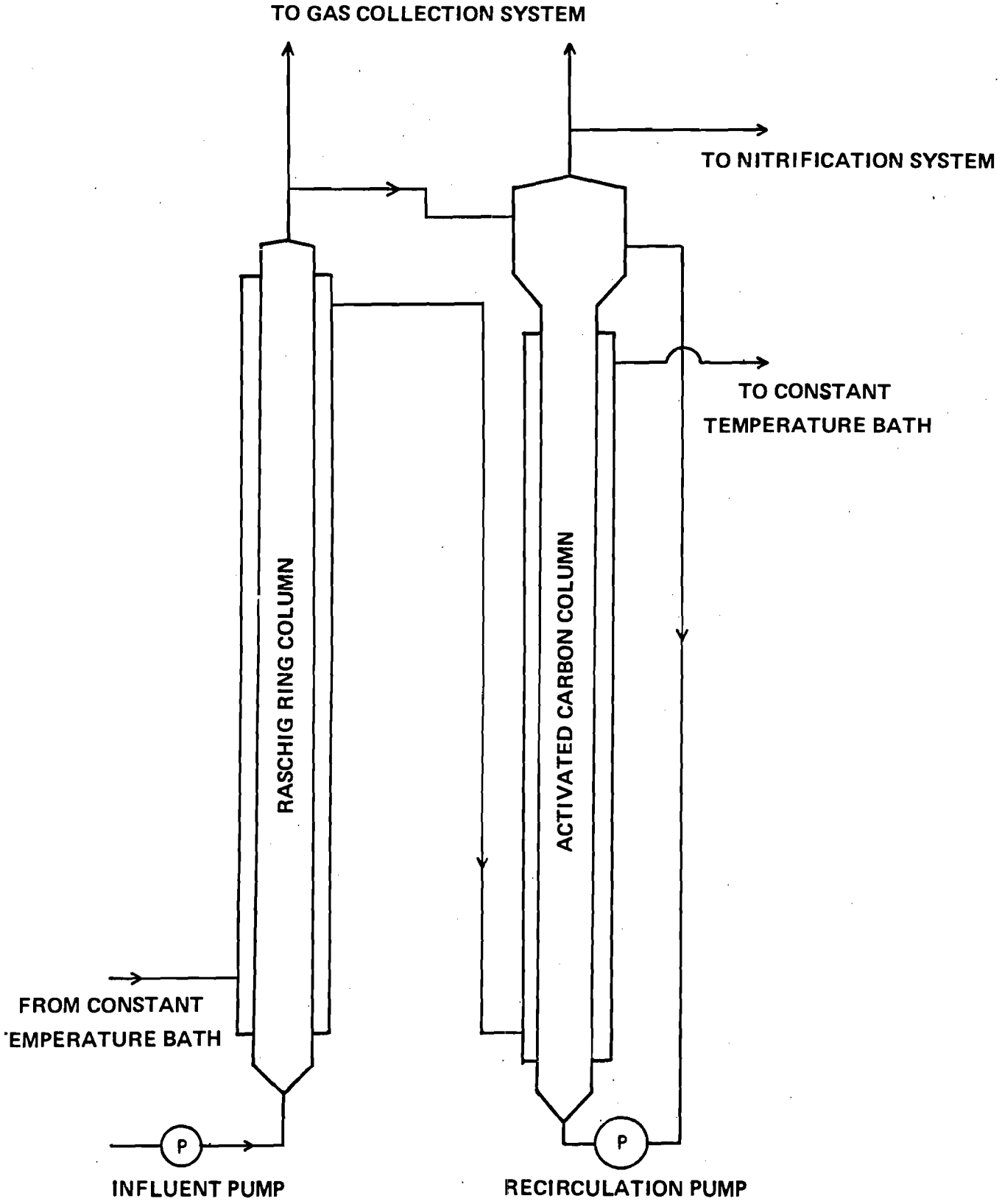

Fig. 58 Two Stage Anaerobic Activated Carbon Filter.

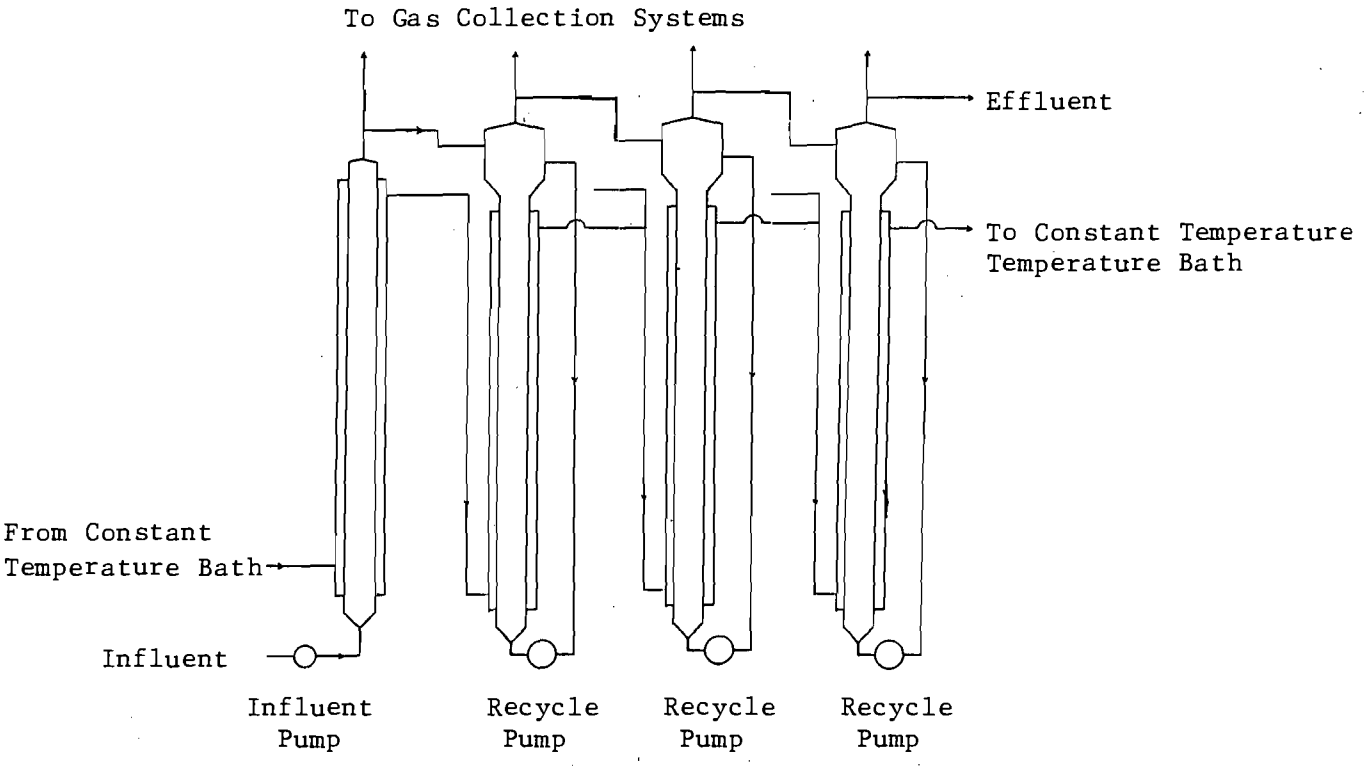

Fig. 59 Anaerobic Activated Carbon Filter in Series.

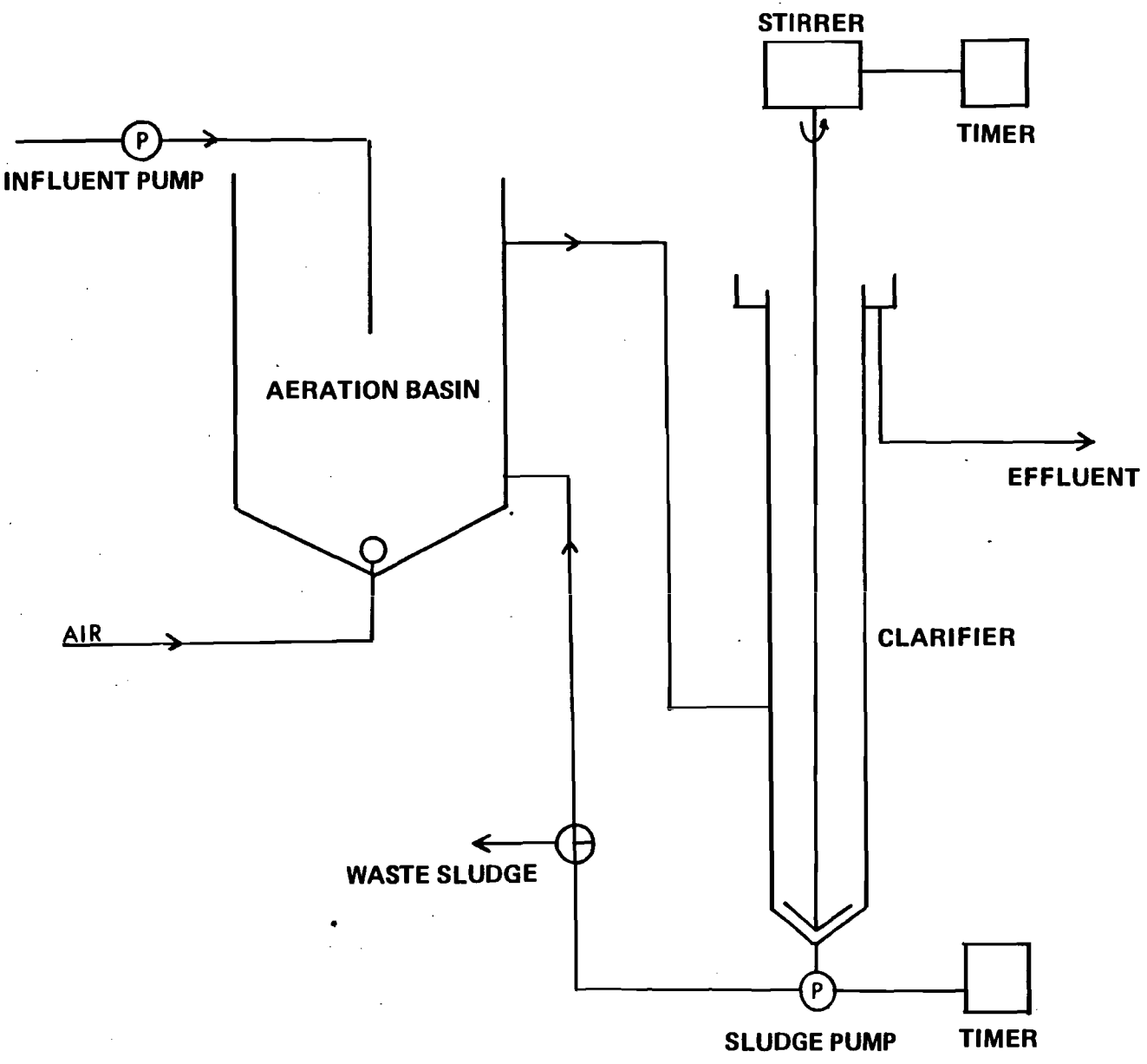

Fig. 60 Biological Nitrification System

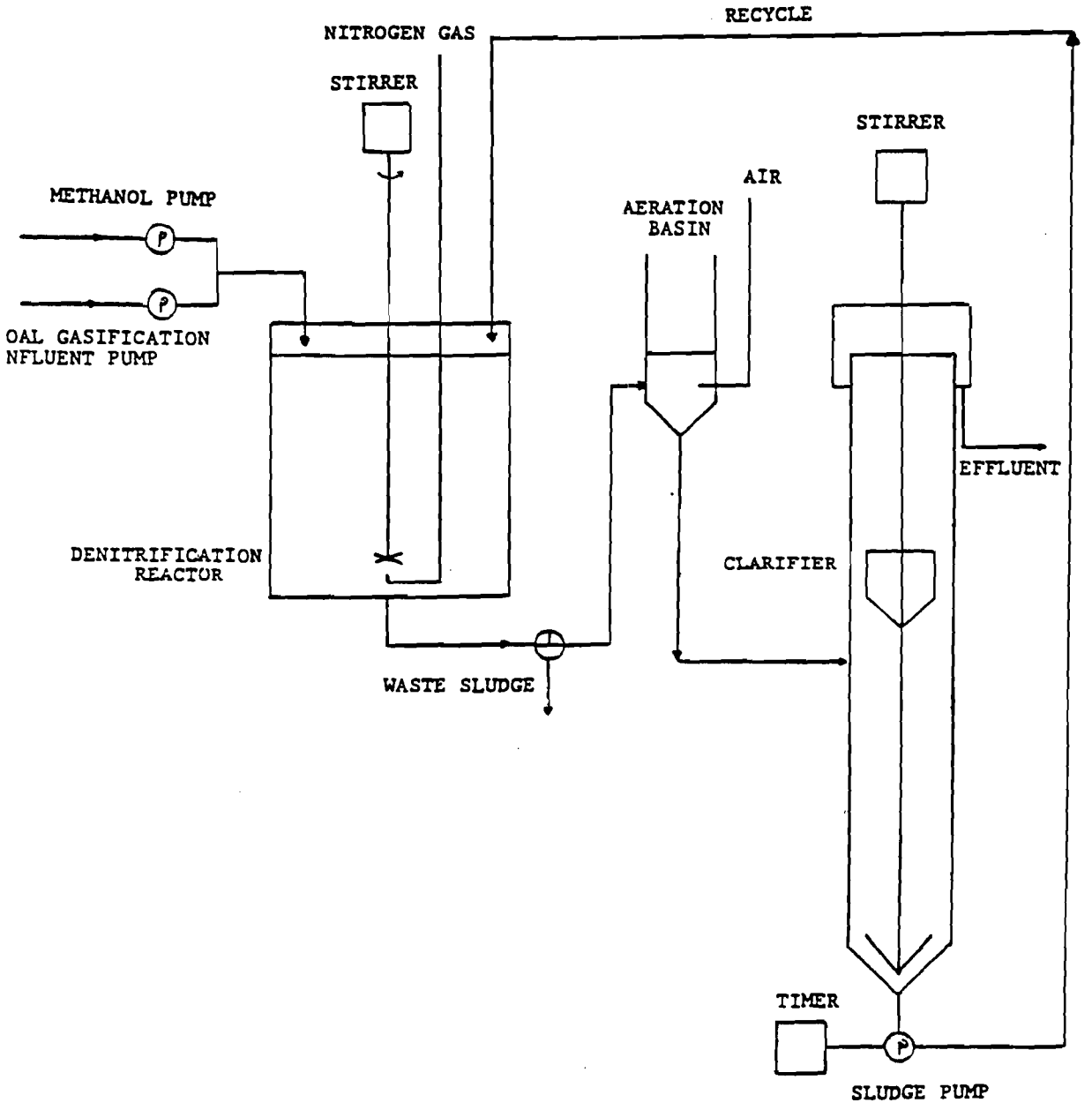

Fig. 61 Biological Denitrification System.

Table 22. Dimensions of the Denitrification Reactor System

Reactor System	Internal Diameter cm	Height cm	Total Volume L	Liquid Volume L	HRT*
Denitrification Reactor	20	38	11.9	10	24
Aeration Basin	6.2	30.5	1.0	0.25	0.5
Clarifier	11.0	100	10.2	10.2	24

*At flow of 10 L/d

reactor was fed into an aeration basin (see dimensions in Table 22). Pressurized air was introduced into the aeration basin through an air diffuser at a rate of 120-160 mL/min. The effluent from this unit then flowed to the clarifier (see dimensions in Table 22). The clarifier had an inverted conical base and settled solids were recycled using a peristaltic tubing pump (Cole Parmer, Chicago, IL). The pump was controlled to recycle solids at a rate of approximately 100 mL/min for three minutes at fifteen-minute intervals resulting in a recycle ratio of 2.9. The clarifier was equipped with two wall scrapers. One was located 37 cm from the top of the clarifier and the second one was at the bottom of the clarifier. In addition, the stirrer was connected to a motor speed controller (Bodine Electric Co., Chicago, IL) and was rotated at a rate of 1 rpm to minimize the quantity of sludge adhering to the walls of the clarifiers or bridging in the conical bottom.

Overall Treatment System

Figure 62 is a schematic diagram for the overall biological treatment system utilized in the study for treating GFSFBG effluent.

Inhibition Studies

Batch inhibition studies were carried out in 125 mL serum bottles using a modified Hungate technique. The bottles were flushed with a carbon dioxide-nitrogen mixture prior to and during filling and inoculation.

Adsorption-Regeneration Studies

Glass columns (Figure 63) (2.5-cm i.d. x 30-cm long) equipped with a positive displacement pump and operated in a upflow mode were used for the adsorption-regeneration cycle studies. Two reservoirs were coupled to the pump via a 3-way stopcock in order to switch from wastewater to regenerant and vice versa without having to shut down the system or interrupt flow through the column.

An automatic time-operated fraction collector was used to obtain samples for analysis.

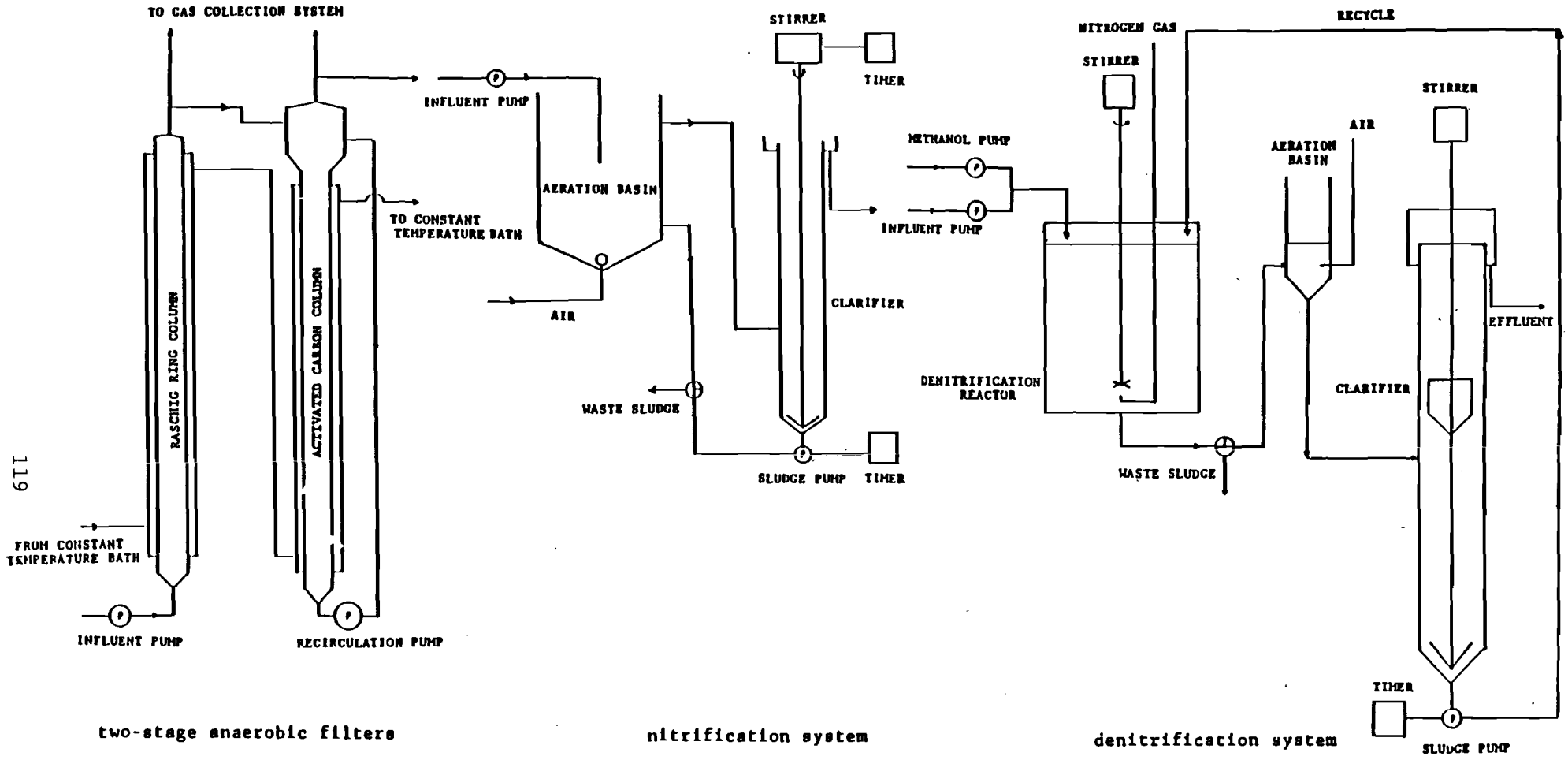

Fig. 62 Overall Processes Used to Treat Coal Gasification Effluent.

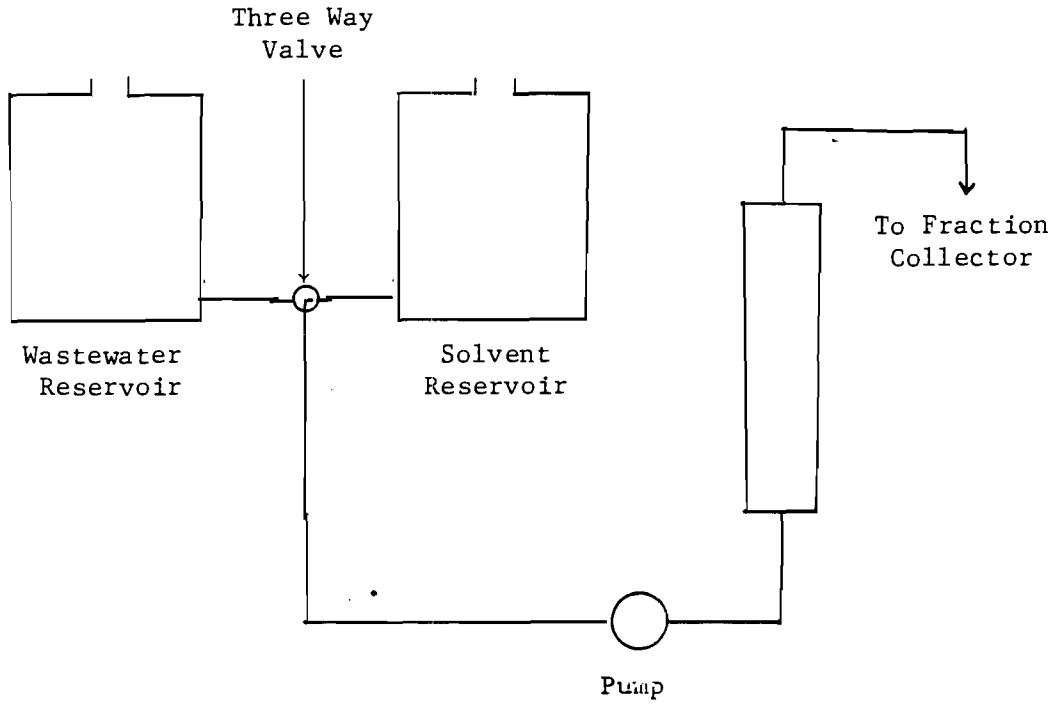

Fig. 63 Carbon Adsorption - Solvent Regeneration System.

APPENDIX C

ANALYTICAL METHODS

Parameter	Method
pH	potentiometric, Standard Methods[35] 423
Alkalinity	Standard Methods 403, endpoint pH = 3.8
ORP	potentiometric, platinum electrode
CN^-	Standard Methods 412E
NH_3-N	Standard Methods 417G
TKN-N	acid digestion (H_2SO_4-$HClO_4$) followed by Standard Methods 417G
PO_4^{-3}-P	Standard Methods 424G
Suspended solids	Standard Methods 209C
Volatile solids	Standard Methods 209D
Total organic carbon	Standard Methods 505A
Chemical oxygen demand	Standard Methods 508A
NO_2^--N	Standard Methods 419
NO_3^--N	Standard Methods 414D
Metals	HNO_3, H_2O_2 oxidation followed by atomic absorption analysis
Phenol, cresols	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 0.1% SP-10000 on 80/100 mesh Carbopack C (Supelco, Inc.). 195°C, nitrogen carrier at 20 mL/min, direct aqueous injection, internal standard benzyl alcohol, FID
Volatile acids	gas chromatography, 1.2-m long glass column, 2-mm i.d., packed with 3.0% Carbowax 20 M, 0.5% H_3PO_4 on 60/80 mesh Carbopack B (Supelco, Inc.). Temperature program 100°C for 2 min to 150°C at 4°C/min and hold for 15 min. Nitrogen carrier 20 mL/min, direct aqueous injection, internal standard 1-butanol or 2-propanol, FID.
Gas composition	gas chromatography, 75-cm long aluminum column, 0.64-cm i.d., packed with 30% DEHS on 60/80 mesh ColumnPak (Fisher Scientific Co.) followed by a 1.8-m long aluminum column 0.48-cm i.d. packed with 60/80 mesh 5A Molecular Sieve (Fisher Scientific Co.) 25°C, Helium carrier 80 mL/min, TCD.

Hydantoins, individual pure solutions	UV/VIS spectroscopy and/or TOC hydantoin, λ_{max} 193 nm; 5-ethyl-5-methyl hydantoin, λ_{max} 193 nm; 5,5-dimethylhydantoin, λ_{max} 198 nm.
Mixtures of hydantoins	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 3% AT-1000 on 100/120 mesh Chromosorb W-HP (Alltech Assoc.) 225°C, nitrogen carrier 40 mL/min, FID, calibration curve.
Other organic constituents	solvent extraction and concentration followed by gas chromatographic separation using mass spectrometry for identification.

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March 17, 1987

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Gasification and Combustion Branch
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Dear Lee:

Enclosed is the camera ready copy of the final report for Contract No. DE-AC18-81FC10297 entitled "Anaerobic Treatment of Gasifier Effluent".

Thank you for your assistance and patience in seeing the report through to the end. I hope we can work together in the future on similar research.

Sincerely,

Wendall H. Cross
Senior Research Scientist

WHC/hb
Enclosure

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DOE/

ANAEROBIC TREATMENT OF GASIFIER EFFLUENT

Final Report

July 1, 1982 - August 31, 1986

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December 1986

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Assistant Secretary for Fossil Fuels

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ABSTRACT

Studies have been conducted to determine the biological treatability of coal gasification effluent for removal of organic carbon and ammonia. The treatment system consisted of a anaerobic activated carbon filter for organic carbon removal followed by a single stage nitrification system followed by a biological denitrification reactor. Dilute (~10%) wastewater was successfully treated over an extended period of time. However, after extended operation (~one year) inhibition of the biological system was encountered. This inhibition could be overcome by periodic replacement of a portion of the granular activated carbon contact media.

Attempts to utilize the anaerobic system to treat solvent extracted ammonia stripped coal gasification effluent to remove substituted hydantoins was of limited success. Removals of 50% of the influent hydantoins were realized but only very small amounts of gas were produced. Apparently the primary removal mechanism was by adsorption on the granular activated carbon.

Batch inhibition studies showed substituted pyridines as the primary inhibitory compounds in the raw wastewater.

Carbon adsorption-solvent regeneration for hydantoin removal did not appear to be a viable treatment alternative due to low adsorption capacities and incomplete regeneration of the activated carbon.

INTRODUCTION

Coal gasification has been regarded as one of the promising technologies in alleviating the nation's energy problems caused by limited supplies of natural gas and petroleum. However, wastewaters generated from some coal gasification processes contain high concentrations of phenols, cresols and ammonia, and lower amounts of cyanide, thiocyanate, and other trace organic compounds. Pretreatment, i.e., solvent extraction followed by steam stripping, is capable of markedly reducing the concentration of phenolic compounds and ammonia. However, there remains in some wastewaters high concentrations of highly water soluble compounds such as substituted hydantoins.

The aerobic activated sludge process has been used to remove organic contaminants from dilute coal gasification wastewaters [1-6]. Most coal conversion technologies incorporate or project the use of aerobic processes as the principle means for treating the residual organic compounds and other impurities present in such wastewater[1]. Such processes are very energy-intensive, with aeration times often exceeding four days. Moreover, instabilities induced by variations in the chemical characteristics of the influent waste stream are often encountered.

In treatability studies conducted on wastewater generated by the Morgantown Energy Research Center fixed-bed coal gasifier, Sack and Bokey[3] observed that major constituents of coal gasification wastewater escape treatment in the activated sludge process even at aeration times exceeding six days. Aromatic amines, thiophenes, and polycyclic hydrocarbons were found to be specially resistant to aerobic treatment while the phenolic content of the treated effluent was invariably in excess of desired levels. Ganczarczyk and Elion[7] obtained similar results from extended aeration treatment of coke plant effluents. Luthy[4] studied a variety of wastewaters generated by coal coking and coal gasification processes and found, with a number of forms of pretreatment, that biological treatment of coal conversion effluents resulted in good removals of biological oxygen demand (BOD), chemical oxygen demand (COD), phenols, ammonia-nitrogen, and cyanide-nitrogen using hydraulic retention times of 2-20 days. However, microbial yields were relatively low, which was attributed to inhibitory constituents in the wastewater. In a similar study, Stamoudis[8] obtained comparable results using hydraulic retention times of two to nine days.

Inhibition of aerobic treatment of coal conversion wastewaters is believed to be due to several constituents present in these wastewaters. Thiocyanate, which is poorly degraded in aerobic biological treatment, exhibits an inhibitory effect on the aerobic biodegradation of phenol[8], while cyanide, thiocyanate, and phenol have been observed to inhibit nitrification of ammonia. Juntgen and Klein[9] have studied the co-inhibition of phenol, thiocyanate, and ammonia during aerobic treatment.

In cross acclimation studies of the treatment of petrochemical wastes in a conventional anaerobic filter, Chou[10] found that the anaerobic environment provided rather rapid acclimation to shock loadings of phenol, catechol, resorcinol, nitrobenzene, and cyanide. Van Velsen[11] demonstrated with treatment of piggery wastes that anaerobic organisms could function efficiently at ammonia concentrations exceeding 6000 mg/L and pH levels of 8.

Lettinga[12] demonstrated that these systems also acclimated rapidly to cyanide.

The feasibility of using anaerobic systems for the treatment of phenol as an alternative to conventional aerobic biological systems has been reported by Hobson et al.[13]. The biokinetics of anaerobic phenol degradation has been studied by Neufeld[14], and Chemielowski[15] has performed specific kinetic research on the anaerobic decomposition of phenol. Healy and Young[16] have demonstrated the process of degradation of phenol and catechol by methanogenic population of bacteria. The anaerobic biodegradability of phenol and catechol has also been confirmed by Khan et al.[17] and Suidan et al.[18]. However, most of these anaerobic biological studies on degradation of phenolic substances involved single synthetic substrates of relatively low concentration. The treatment process used in this study combines the advantages of the energy-efficient anaerobic filter process developed by Young and McCarty[19] and later modified by Chian and DeWalle[20]. Recirculation of the effluent and the adsorptive capacity of activated carbon for the extended detention of less readily biodegradable compounds were originally reported by Khan et al.[17] for the anaerobic degradation of phenols. Recent work by Suidan[21-22] has shown the applicability of anaerobic filters for treating coke wastewaters.

Activated carbon is often used as a contact medium for biological treatment systems since it has the excellent characteristics of being light-weight, having a large surface area, a large void volume, and surface properties that are conducive to the growth of microorganisms. The activated carbon may also adsorb inhibitors to microbe metabolism which would allow the biological treatment process to continue even though inhibitory agents are present in the waste stream. In this regard, it is particularly useful as a medium for anaerobic filters since anaerobic treatment processes are relatively sensitive to inhibition. This report is based on results obtained from anaerobic filters studied as a treatment alternative for the water quench waste stream from a pilot-scale coal gasifier operated by the former Grand Forks Energy Technology Center (GFETC) (currently the University of North Dakota Energy Research Center (UNDERC)).

The UNDERC gasifier is a slagging fixed-bed unit.[23] Coal is gravity fed from hoppers at the top of the gasifier, and is dried, devolatilized and finally combusted and gasified as it descends in the reactor. The non-combustible portion (ash) of the coal is removed from the unit as slag, while the product gas flows upward in the reactor, countercurrent to the coal, and exits at the top of the vessel. An oxygen and steam mixture at about a one to one molar ratio is introduced to the reactor through four tuyeres above the hearth plate. With high moisture lignite, a gas offtake temperature of 325°F is realized. The gasification system can operate at pessures up to 600 psi. The hot product stream enters a water quench spray cooler where soluble gases and devolatilization products are removed. The soluble gases removed include NH_3, CO_2, HCN, and H_2S while the devolatilization products include tars, oils, and water vapor. The product gas then is processed through an overhead gas cooler where additional light oils and water vapor are removed.

The wastewater streams in the gasification process are the gas liquors from the spray cooler and light oils and water vapor from the overhead gas cooler. Both streams are sent to a tar/oil/water separator where oils and tar are gravity separated. Most of the work reported herein was performed on water which had been obtained from the tar/water separator.

UNDERC has the capability to further treat the wastewater from the tar/water separation unit. Sand filtration is used to remove residual tar, followed by solvent extraction and steam stripping. Solvent extraction employs diisopropylether to remove dissolved organic compounds. Steam stripping is utilized to remove ammonia and acid gases. A portion of the study reported here utilized water resulting from the solvent extraction steam stripping operation.

RESEARCH OBJECTIVES

Objectives of the overall research project included:

1. A study of the treatability of raw GFSFBG effluent using a two stage anaerobic activated carbon filter and determination of maximum loading rates and the effect of recycle rate on treatment performance.

2. Identification of compounds inhibitory and/or toxic to the biological treatment system.

3. Determine the applicability of biological treatment for the removal of ammonia from the anaerobically treated effluent (nitrification-denitrification).

4. Determine the treatability of solvent extracted ammonia stripped wastewater for removal of hydantoins using anaerobic activated carbon filters.

5. Determine the adsorption capacity of granular activated carbon for hydantoins.

6. Investigate the solvent regeneration of granular activated carbon saturated with hydantoins.

MATERIALS AND METHODS

Wastewater Sources

All wastewater was produced at the University of North Dakota Energy Research Center (UNDERC) and shipped to the Georgia Institute of Technology (GIT) via refrigerated trucks. Upon receipt at GIT the wastewater was stored frozen in five gallon plastic containers. Individual containers were thawed as needed, composited in fifty gallon batches, diluted and used in the project. Two different batches of gasifier effluent were used in the study. These were designated by UNDERC as RA-52 and RA-87. A separate batch of pretreated (solvent extracted-steam stripped) wastewater was utilized for the feasibility study of the anaerobic treatment of hydantoins and the adsorption-solvent regeneration of granular activated carbon.

Results of the analysis of the raw gasifier wastewater are presented in Tables 1 and 2 and the pretreated wastewater characteristics are presented in Table 3.

Biological Treatment Systems and Carbon Adsorption-Regeneration System

Schematic diagrams, physical dimension, and operating characteristics of all systems used in the study are given in Appendix A.

Analytical Methods

Specific methods of analysis used for the evaluation of all samples are given in Appendix B. In general all samples were filtered through a 0.45 μM membrane filter prior to analysis.

Table 1. Characteristics of Raw UNDERC Coal Gasification Effluent (Average of Six Samples)

	Concentration[a]
pH	8.2
Total organic carbon (TOC)	11,900
Chemical oxygen demand (COD)	26,900
Total alkalinity (as $CaCO_3$)	25,000
Total suspended solids (TSS)	3,670
Total volatile solids (TVS)	3,180
Total volatile acids (as CH_3COOH)	460
Phenol[c]	5,600
o-Cresol[c]	640
m-Cresol[c]	930
p-Cresol[c]	910
NH_3-N	5,300
CN^-	140
SCN^-	150
S^{-2}	BDL[b]
Metals	
Chromium	BDL
Zinc	BDL
Nickel	BDL
Copper	BDL
Iron	5.5
Manganese	BDL

[a]mg/L except pH.
[b]Below detection limit.
[c]By gas chromatographic analysis.

Table 2. Minor Constituents of UNDERC Gasification Effluent

Compound	Concentration (mg/L)
Acid Fraction	
2,6-Dimethylphenol	12
2-Ethylphenol	50
2,4-Dimethylphenol+2,5-Dimethylphenol	358
3,5-Dimethylphenol+3-Ethylphenol+4-Ethylphenol	968
2,3-Dimethylphenol	40
Dimethoxybenzene or C_2-Benzenediol	46
3,4-Dimethylphenol	158
C_3-Phenol	10
C_3-Phenol	8
C_3-Phenol	20
C_3-Phenol	4
C_3-Phenol	24
C_3-Phenol	20
Naphthol	4
Neutral Fraction	
Benezene	1.1
Toluene	1.4
Cyclopentanone	0.8
Aliphatic hydrocarbon	0.3
C_1-Cyclopentanone	0.3
Ethylbenzene	0.1
o-Xylene	0.5
m- and p-Xylene	0.3
Methoxybenzene	0.2
Benzonitrile	0.7
C_3-Benzene	0.6
C_1-Methoxybenzene	0.5
C_3-Benzene	2.0
Naphthalene	0.7
C_1-Naphthalene	2.1
Indole	1.0
C_1-Naphthalene	0.9
C_2-Benzaldehyde	2.2
Acenaphthylene	0.6
1,1'-Biphenyl	0.4
Dihydroacenaphthylene	0.3
Dibenzofuran	0.5
Fluorene	0.5
C_3-Napthalene	0.1
C_1-Dibenzofuran	0.2
Phenanthrene	0.6
Anthracene	0.2
Fluoranthene	0.2
Pyrene	0.1
C_1-Pyrene	0.04

Compound	Concentration (mg/L)
Base Fraction	
Pyridine	4.62
2-Picoline	3.71
3-Picoline+4-Picoline	2.53
C_2-Pyridine	1.4
C_2-Pyridine	0.29
C_2-Pyridine	1.06
C_2-Pyridine	0.32
C_2-Pyridine	0.12
C_2-Pyridine	0.04
C_2-Pyridine	0.07
Aniline	1.10
C_3-Pyridine	0.16
C_2-Pyridine	0.12
C_3-Pyridine	0.20
C_3-Pyridine	0.02
C_3-Pyridine	0.02
C_3-Pyridine	0.01
C_3-Pyridine	0.03
C_1-Aniline	0.53
C_1-Aniline	0.18
C_2-Aniline	0.01
C_3-Pyridine	0.06
C_2-Aniline	0.03
C_3-Pyridine	0.01
Quinoline	0.49
Isoquinoline	0.01
C_1-Quinoline	0.08
C_1-Quinoline	0.03
C_1-Quinoline	0.02
C_1-Quinoline	0.01
C_1-Isoquinoline or C_1-Quinoline	0.01
C_1-Quinoline	0.01
C_1-Isoquinoline	0.01
C_2-Quinoline	0.01
C_2-Quinoline	0.02

Table 3. Pretreated Wastewater Characteristics[c]

Constituent	Concentration[a]
pH	8.9
TOC	1,700
COD	5,700
Total alkalinity (as $CaCO_3$)	1,500
Methanol	230
Ethanol	BDL[b]
Acetone	10
2-Propanol	BDL
Acetonitrite	2
Diisopropylether	BDL
1-Propanol	BDL
Propionitrite	BDL
Phenol	160
o-Cresol	BDL
m-Cresol	BDL
p-Cresol	BDL
5,5-Dimethylhydantoin	2,140
5-Methyl-5-ethylhydantoin	490
Total volatile acids (as CH_3COOH)	BDL
NH_3	560
Sulfide	8
Cyanide	39
Thiocyanate	210

[a] mg/L
[b] Below Detection Limit (Detection Limit ~10 mg/L)
[c] Solvent Extracted-Ammonia Stripped

Feed Substrate. The feed substrate employed in this study was a dilute solution of coal gasification wastewater having a total organic carbon (TOC) concentration up to approximately 1000 mg/L. This corresponds to approximately 10% wastewater in the feed.

During the initial acclimation phase, glucose was also added to some systems to provide a readily available carbon source for bacterial growth. Unlike the procedure reported by Khan at al.[17], no vitamins or trace metals were added but a mixture of sodium and potassium phosphates were included to supplement the wastewater with phosphorus.

Process Monitoring. Daily checks of pump flow rates, carbon bed expansion, feed reservoir volume, pH, and gas production were made for each system. Weekly determination of total organic carbon, chemical oxygen demand (COD), oxidation reduction potential (ORP), alkalinity, total volatile acids, phenol, and gas composition were performed on influents and effluents from the anaerobic systems. The data were used to assess the performance of each unit in terms of removal efficiency of organic contaminants and the production and conversion of specific compounds, such as organic acids and phenol.

Anaerobic Treatment Systems

During the course of the project four anaerobic treatment systems were utilized. The system configurations were as follows:

System I - anaerobic upflow Raschig ring packed column followed by an anaerobic fluidized activated carbon filter.
System II - identical to System I.
System III - A single anaerobic fluidized activated carbon filter.
System IV - three anaerobic fluidized activated carbon filter in series.

Details concerning the construction of the individual columns are given in Appendix A.

Systems I and II were started simultaneously, allowed to acclimate (Phase I), operated at pseudo-steady-state (Phase II) until failure occurred. System III was started approximately 90 days after System I and II and was operated with granular activated carbon replacement based on the results obtained with Systems I and II. System IV was started approximately one year after System I and II and was studied as an alternative to granular activated carbon replacement within a single reactor.

RESULTS AND DISCUSSION

Anaerobic Filters

The four pilot-scale two-stage anaerobic Raschig ring and granular activated carbon filter systems used in this study were operated at empty-bed hydraulic retention times of 24 hours in each column. The Raschig ring packed fixed-bed reactor was operated in a plug-flow mode, whereas the granular activated carbon reactor was operated in a fluidized (well mixed) mode. The latter was accomplished by means of effluent recycle at an upflow rate of 5 gpm/ft^2 (13.3 m^3/m^2/h). As indicated in Table 4, Systems I and II were started on Day 0 and operated approximately one year; Systems III and IV were started on Days 87 and 380 respectively (Table 5).

Phase I - Acclimation

During the 147 days of phase I, the first-stage Raschig ring packed column was seeded with approximately 4 L of settled digested sludge (ca.5-6%) solids collected from a local sewage treatment plant (R. M. Clayton Plant, Atlanta, GA). The procedure for seeding the Raschig ring packed column was based on previous experience with difficulty encountered in directly establishing a viable microbial population in the fluidized carbon bed. The procedures for acclimating the system receiving coal gasification wastewater are given in Table 4. As shown, the substrates fed to the system were maintained at 1000 mg/L TOC. During this phase of the study, glucose was added to one reactor system to facilitate rapid accumulation of a bacterial population producing methane gas. An increasing concentration of wastewater with a concomitant decrease of the glucose concentration was added to the feed to enhance acclimation of the microorganisms capable of degrading the coal gasification wastewater. The use of this start-up procedure was found to have little effect on the rate of acclimation of the sludge toward degrading coal gasification wastewaters in either system.

Phase II - Pseudo-Steady-State Operation

During the 47 days of phase II (Day 147-194), both systems were operated under identical conditions with a feed consisting of only diluted coal gasification wastewater (ca. 10% raw wastewater) and phosphates. Feed flow rates were maintained at 10 mL/min (14.4 L/d) to each system and the systems were monitored to assess their performance.

Chemical oxygen demand and TOC removals during this period, indicated in Figures 1-4, exhibit similar performance for both systems, with COD removals increasing with time. The COD removals averaged 77.6 and 87.1% for systems I and II, respectively, while corresponding TOC removals averaged 73.0 and 78.1%. Phenol removals, shown in Figures 5 and 6, were in excess of 90% for both systems. Phenol removals decreased somewhat after day 147, when the overall loading on the system increased, and then began increasing again with final effluent concentrations in the range of 20-40 mg/L. Only 10-20% of the phenol was removed in the first-stage Raschig ring column, with the remainder being removed in the second-stage granular activated carbon column.

Removal of cresols was also monitored during pseudo-steady-state Operations. Overall removal efficiencies were 99.9 and 99.4% for systems I and II, respectively, with approximately 58% being removed by the Raschig ring column and 41% by the granular activated carbon columns.

Table 4. Anaerobic Reactor Systems I and II, Feed Composition

Phase I	Duration Days	Flow Rate ml/min	System I		System II	
			Wastewater mg/L TOC	Glucose mg/L TOC	Wastewater mg/L TOC	Glucose mg/L TOC
A[a]	1-50	10	500	500	500	500
B	50-70	10	800	0	800	0
C	70-84	7	800	0	700	300
D	84-112	7	1,000	0	700	300
E	112-147	7	1,000	0	800	200
Phase II	147-194	10	1,000	0	1,000	0

[a]Designation of incremental substrate changes.

Table 5. Anaerobic Reactor Systems III and IV, Feed Composition

System III - One AFACF[a] with cyclic carbon replacement
System IV - Series of three AFAC Filters

SYSTEM III				SYSTEM IV			
DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l	DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l
87-133	10	500	500	380-440	5.0	0	1000
134-147	10	400	600	441-455	6.0	0	1000
148-167	10	300	700	456-466	7.5	0	1000
168-195	10	200	800	467-575	10.0	0	1000
196-216	10	100	900				
217-550	10	0	1000				

[a]Anaerobic Fluidized Activated Carbon Filter

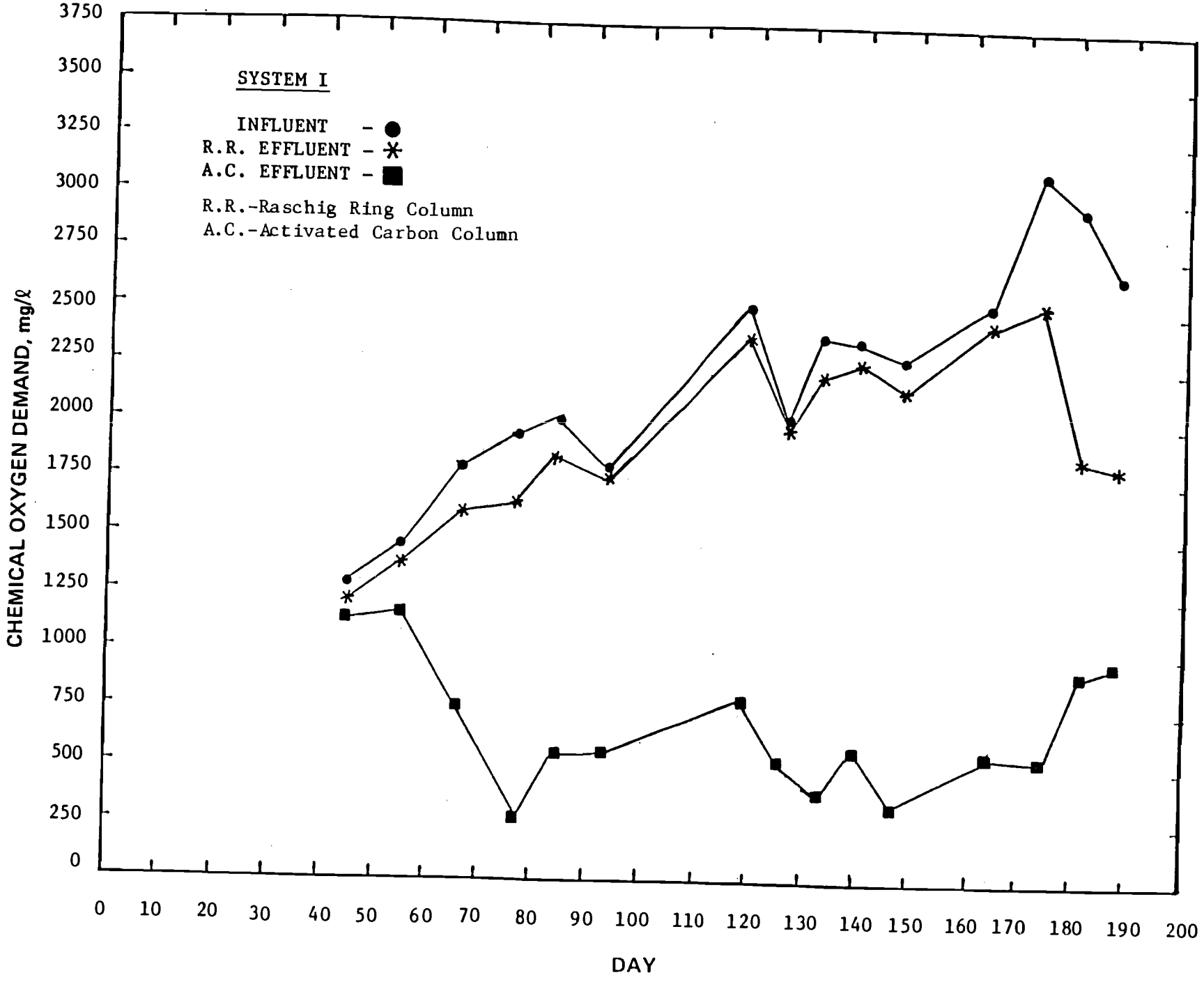

Fig. 1 COD Removal System I.

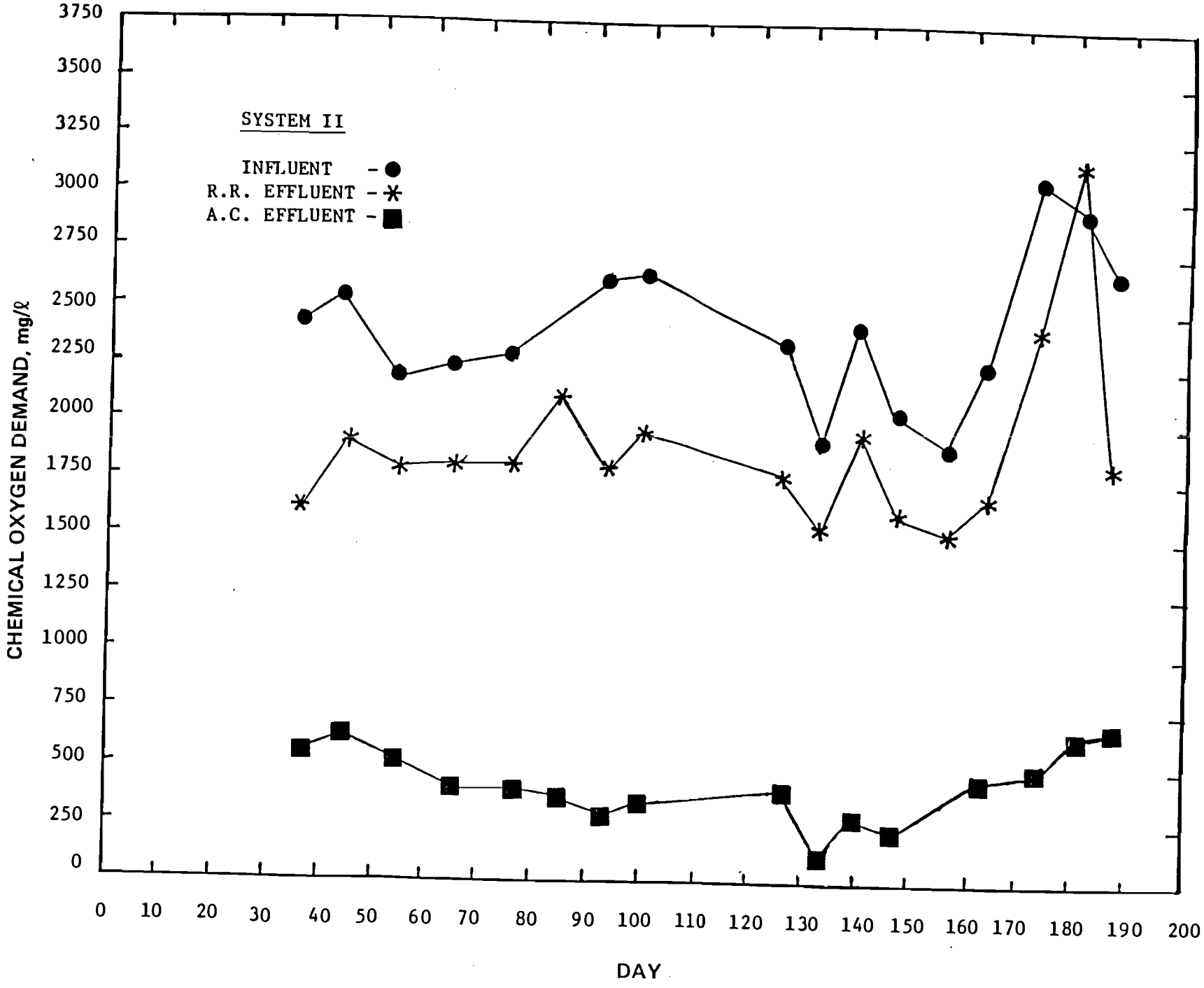

Fig. 2 COD Removal System II.

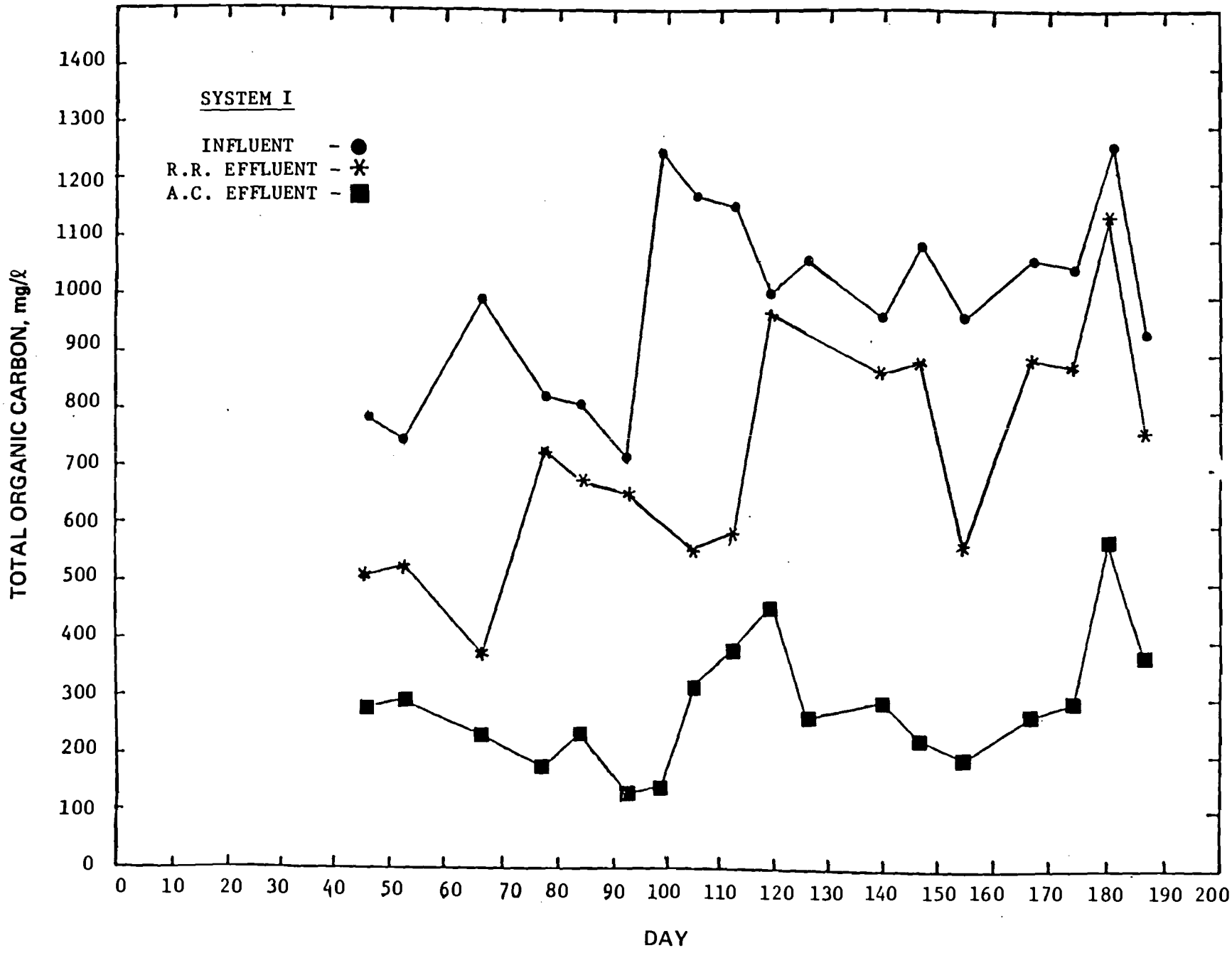

Fig. 3 TOC Removal System I.

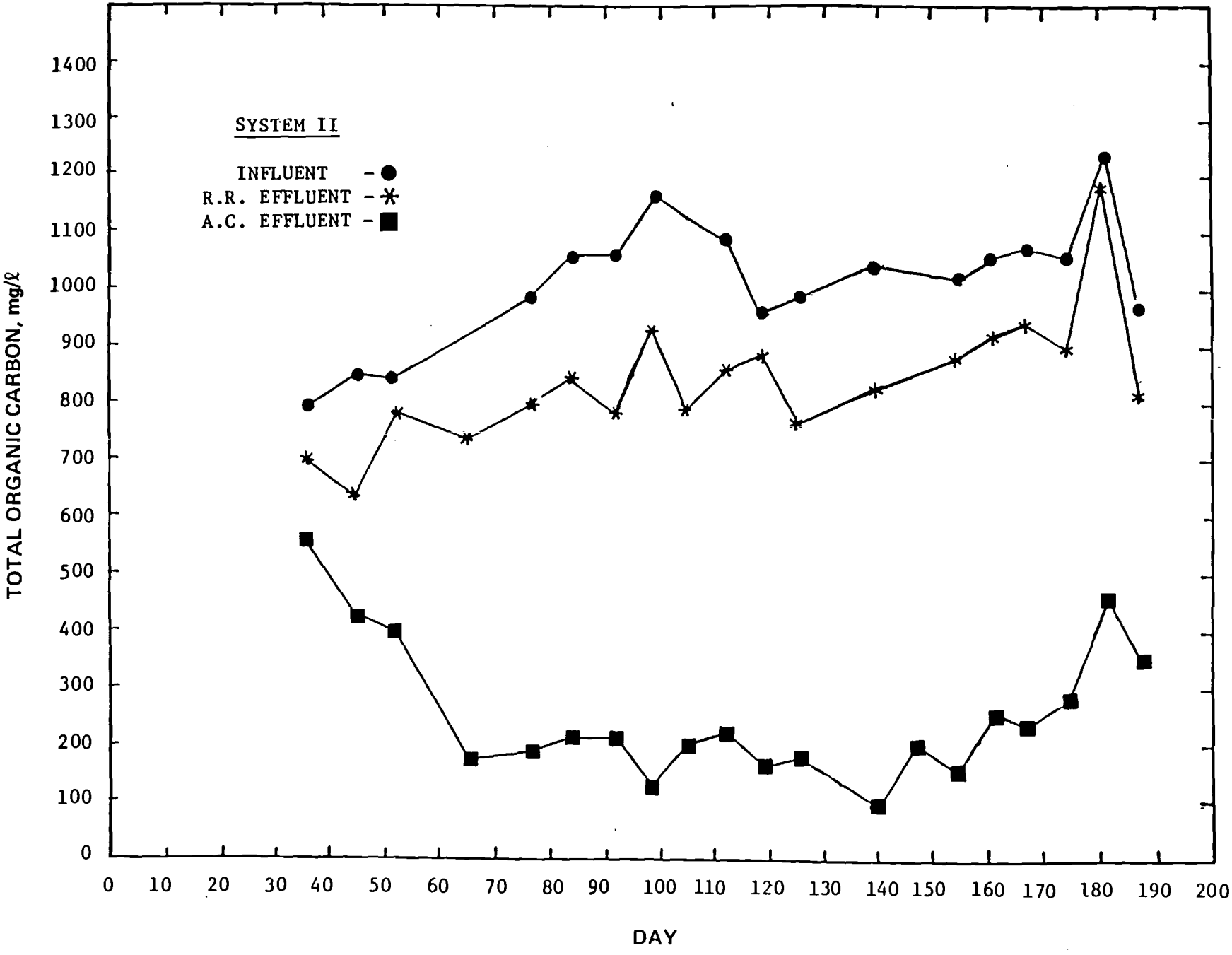

Fig. 4 TOC Removal System II.

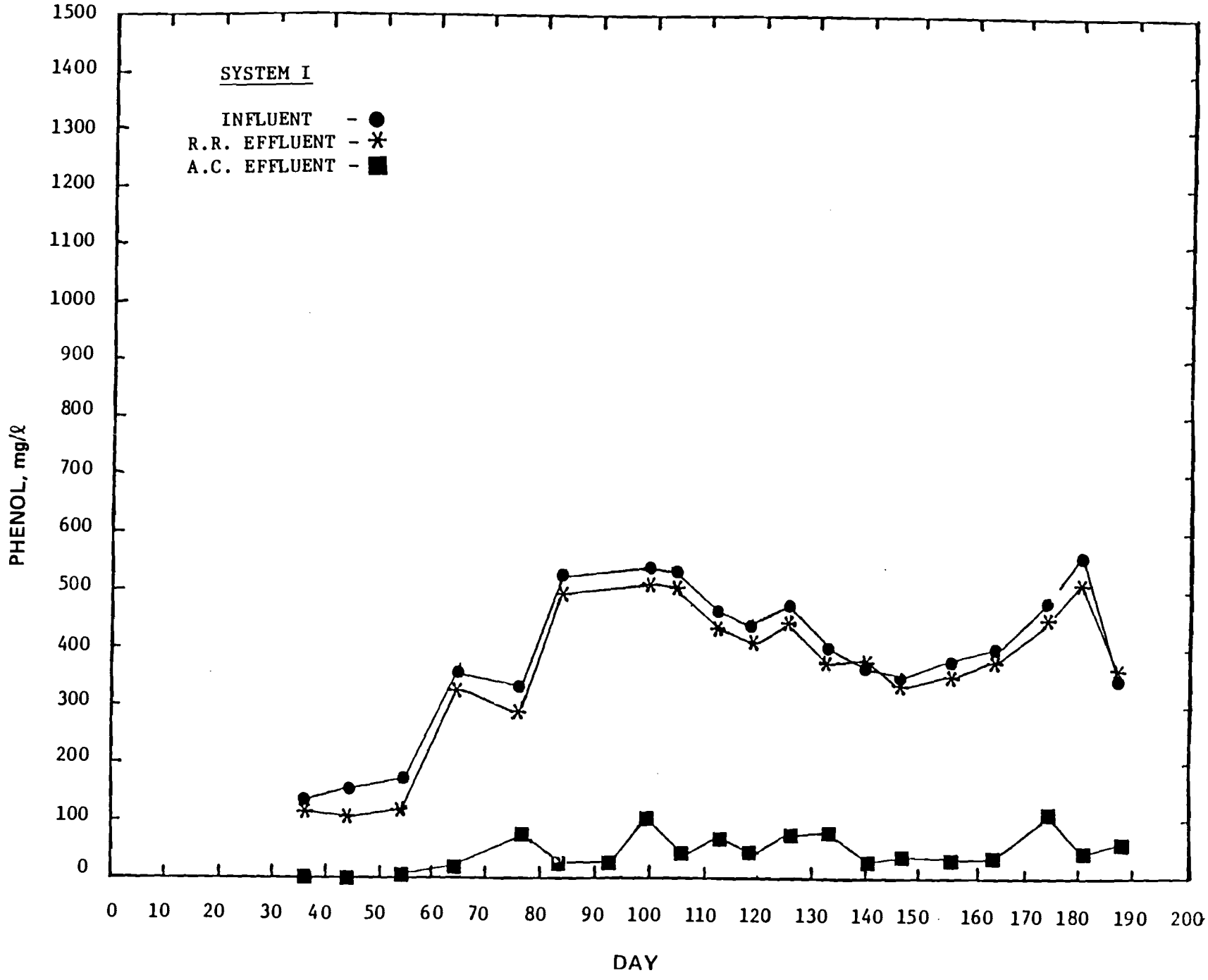

Fig. 5. Phenol Removal System I.

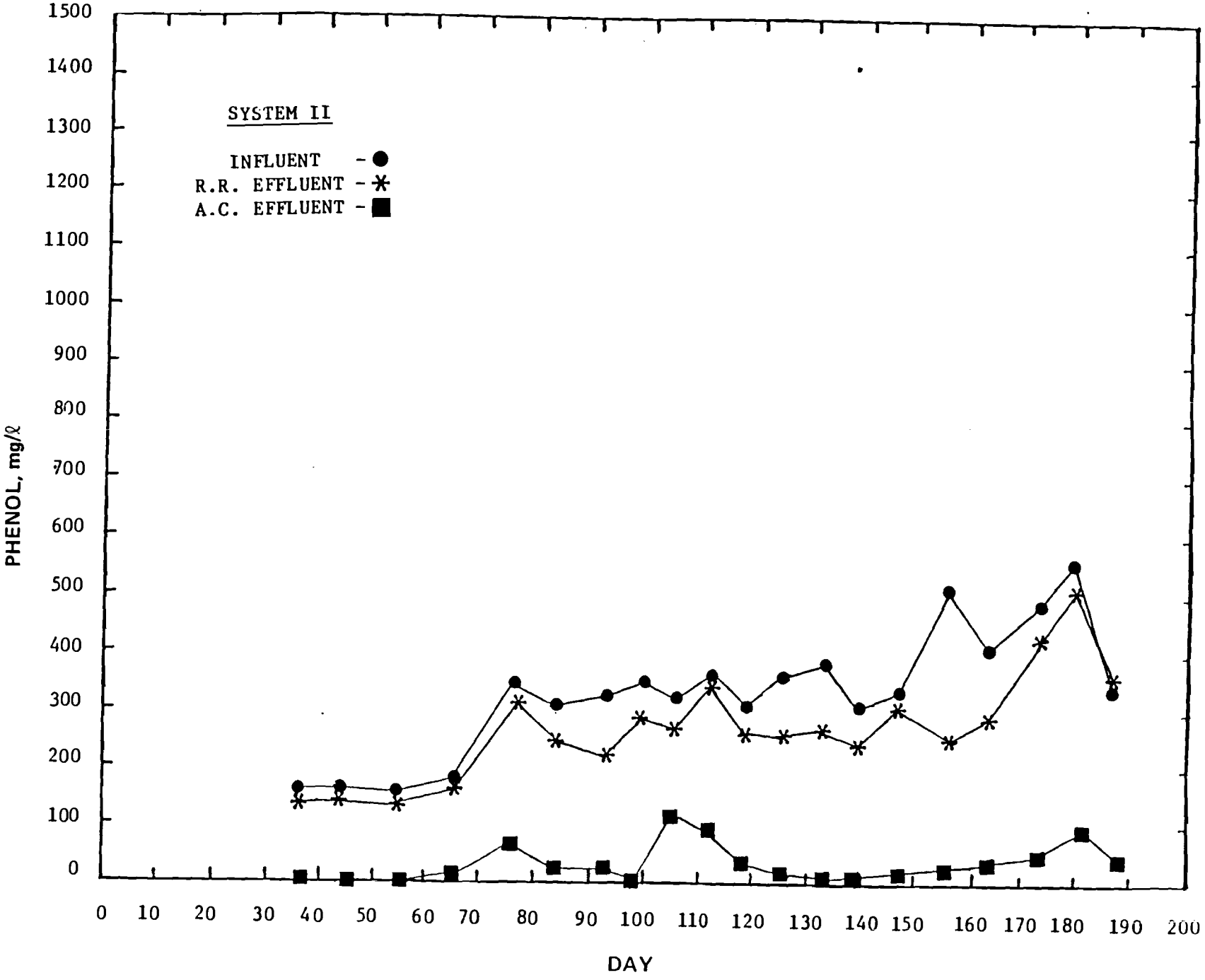

Fig. 6 Phenol Removal System II.

Volatile fatty acids concentrations, shown in Figures 7 and 8, indicate fluctuations in concentration during the acclimation period due to changes in loading and other operational stresses imposed on the systems. However, there was an overall decrease in the acid concentrations as the systems became acclimated and more completely converted the acids to methane and carbon dioxide. Levels of total volatile fatty acids in the final effluent were on the order of 100 mg/L.

Gas production, shown in Figures 9 and 10 continued to increase during the acclimation period until rates of 5.7 L methane/day for system I and 3.6 L methane/day for system II were achieved. The quantity of methane being produced by system I was slightly in excess of that calculated from the anaerobic degradation of the influent phenol, while the amount produced by system II was slightly less. However, no correction has been made for conversion of substrate to biomass or for the solubility of methane in water. Approximately 86% of the methane produced was generated by microbial activity within the granular activated carbon columns.

Suspended solids in the effluent of the granular activated carbon columns were on the order of 20 and 40 mg/L for systems I and II, respectively.

CONCLUSIONS

Wastewater from the UNDERC coal gasification process are amenable to treatment by a two-stage anaerobic filter packed with Raschig rings and granular activated carbon. Results indicate that good removal of the major wastewater constituents were obtainable using a dilute wastewater (ca. 10% raw wastewater) with a total empty-bed retention time of approximately two days. At a loading of 2.5 kg COD/m^3d the two-stage system had removal efficiencies of 87% COD, 78% TOC, 93% phenol, and 99% cresols during pseudo-steady-state operation. No apparent inhibition was observed under the stated operating conditions.

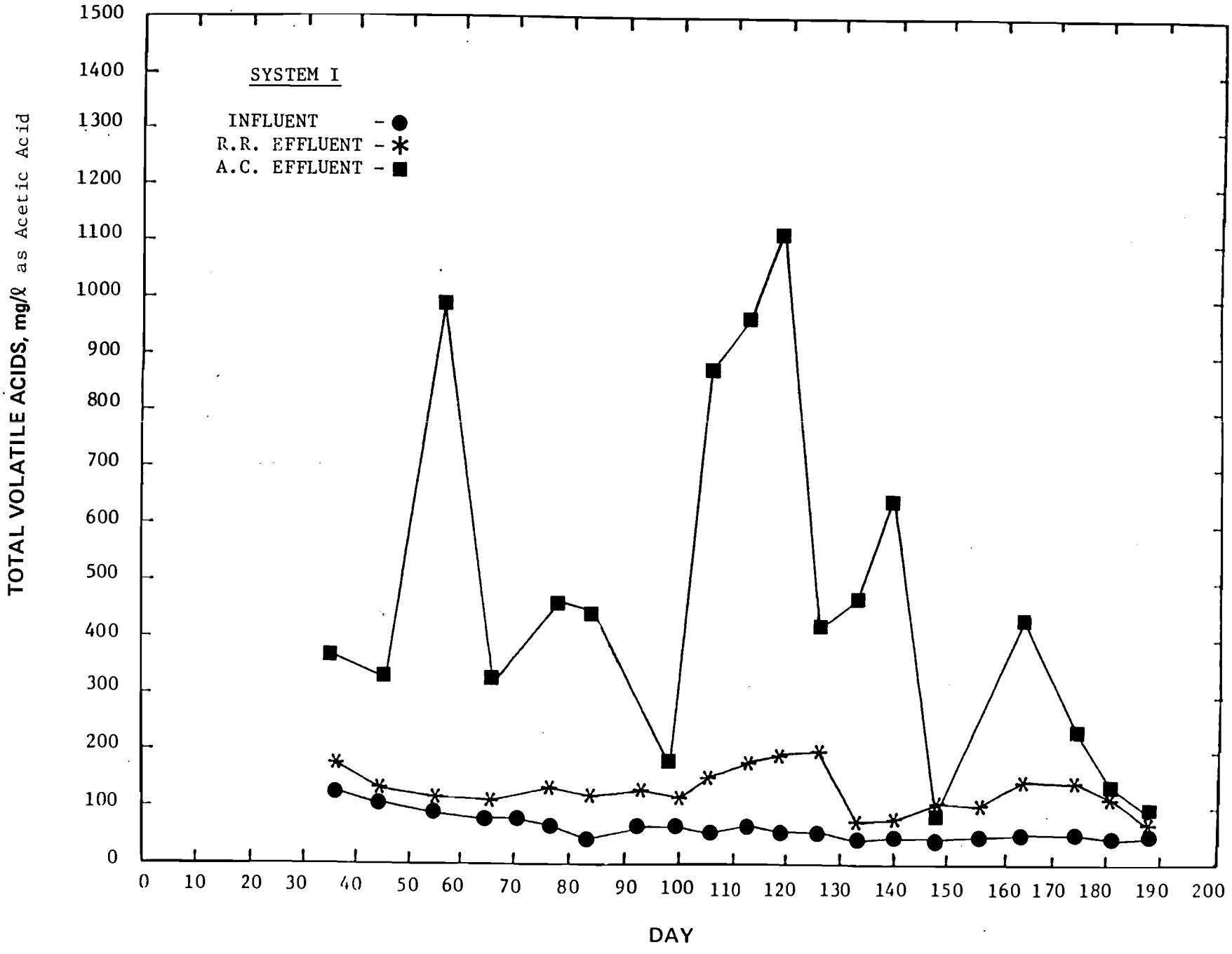

Fig. 7 Total Volatile Acids System I.

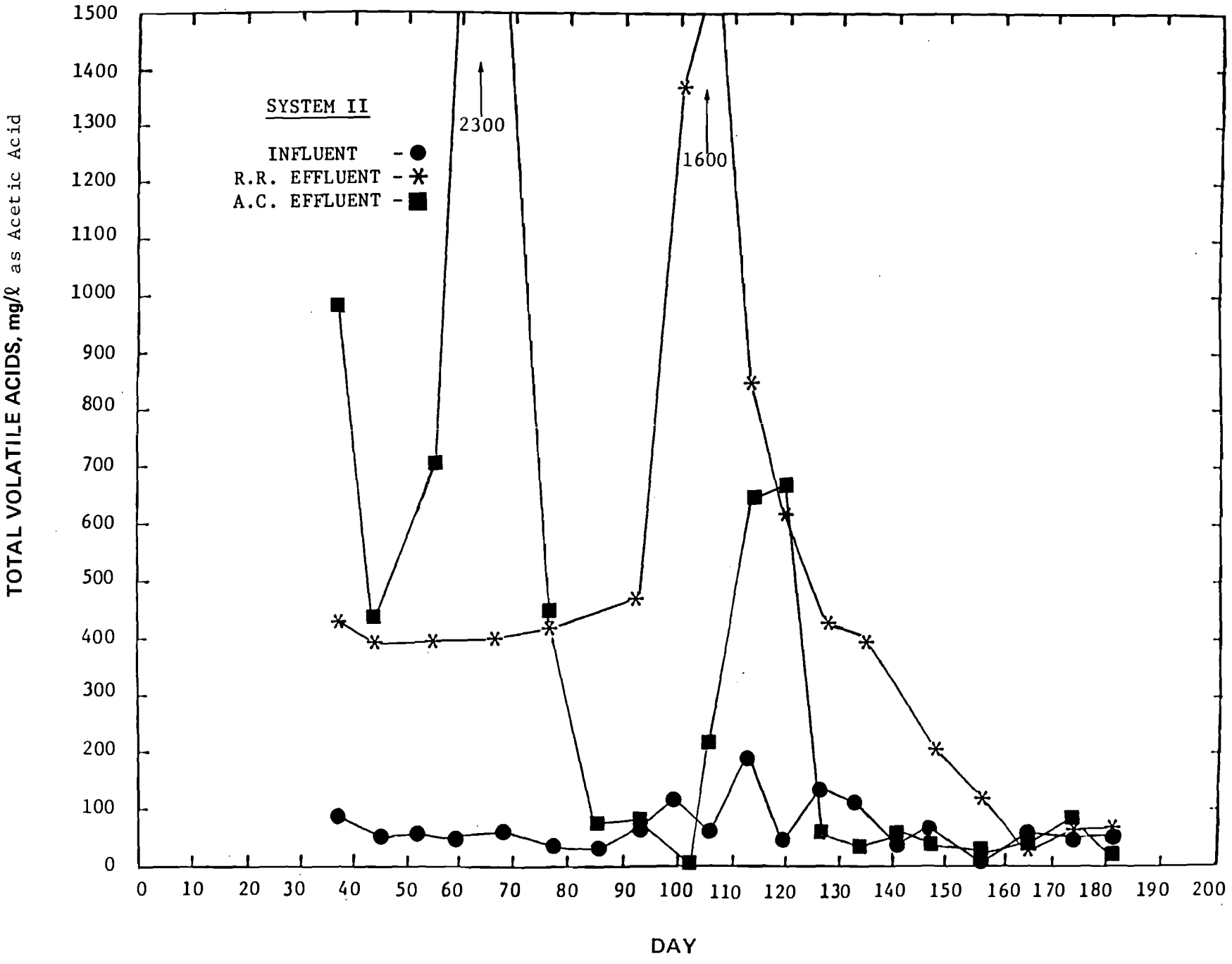

Fig. 8 Total Volatile Acids System II.

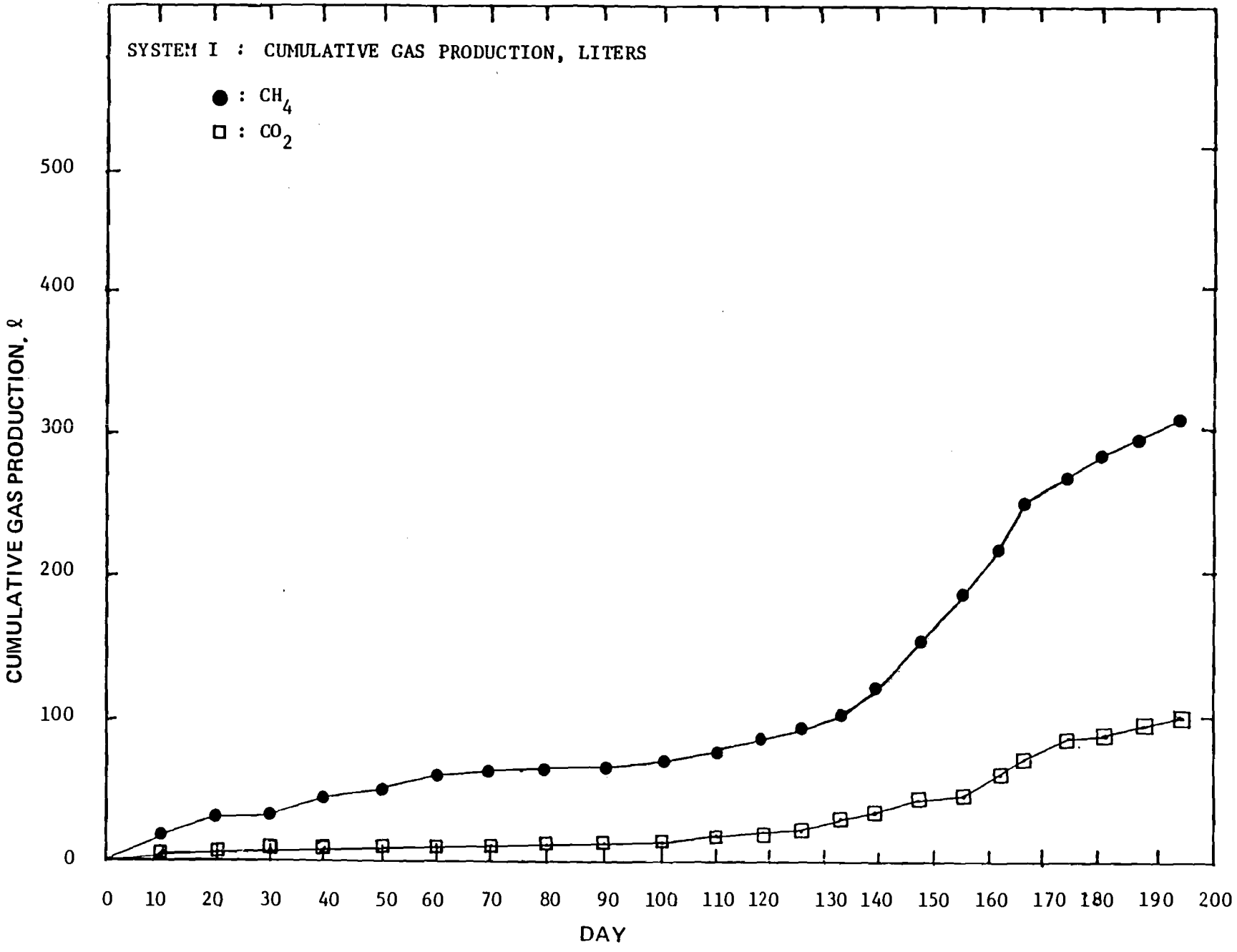

Fig. 9 Gas Production System I.

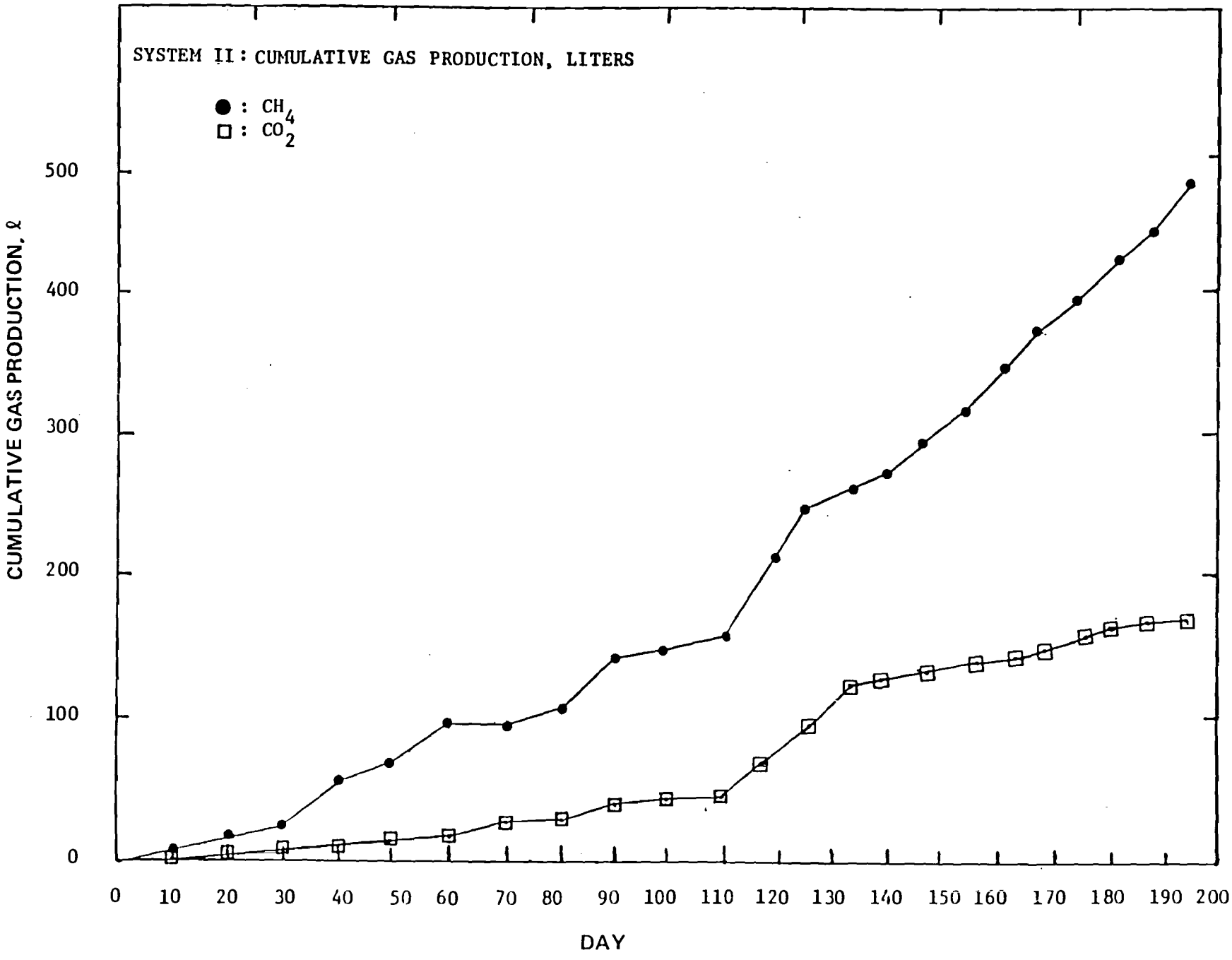

Fig 10 Gas Production System II

CARBON REPLACEMENT DUE TO SYSTEM INHIBITION

The study reported herein establishes the relationship between adsorption provided by the activated carbon and the improvement in biological conversion of coal gasification wastewaters. A mutually beneficial relationship has been observed wherein adsorption serves as an *in situ* pretreatment which promotes conditions suitable for biological growth; the ensuing biological activity extends the life of the carbon via bioregeneration. An understanding of this relationship was considered central to successful operation of the process and for approaching optimum process performance.

Process Inhibition, System II - Carbon Solvent Extraction

Figure 11 shows the variability in performance as measured by gas production and organic carbon removal of system II during its period of operation. On day 195, the influent TOC to the reactor was increased from 1000 mg/L to around 1500 mg/L by decreasing the wastewater dilution from approximately 10:1 to approximately 8:1. Process performance declined rapidly and failed to recover despite attempts at pH control and an ultimate reduction in the organic load. The ensuing search for the cause of process failure led to solvent extraction of the activated carbon with dioxane and dimethylformamide. Subsequent GC/MS analysis of the solvent extract revealed an accumulation of cresols and C-2 substituted phenols on the carbon as compared to the influent, Table 6 and Table 7.

Examination of Figure 11 reveals that the beginning of process failure appeared to coincide with carbon saturation as indicated by the almost complete breakthrough of cresols at about day 200. This also occurred immediately after the increase in loading, influent TOC increased from 1000 mg/L to 1500 mg/L. Therefore it was not possible to clearly distinguish whether the process failed due to overloading, inhibition due to some component remaining in solution in the absence of adsorptive removal, or a combination of the two.

Process Inhibition, System III - Carbon Cycling for in situ Pretreatment

System III was carefully monitored in terms of gas production and removal efficiencies with speculation that an inhibitory pollutant might appear at around the time of carbon saturation. Figure 12 shows a slow but constant decline in process performance following phenol breakthrough around day 125, and becoming appreciably more notable following the beginning of cresol breakthrough at around day 210. Particularly poor performance was observed in system III around days 330 and 440. Figure 12 shows an accumulation of volatile acids under these conditions, which suggests that the methanogens are inhibited first thus preventing conversion of the volatile acids to methane and carbon dioxide.

Soon after cresol saturation, COD removal efficiencies declined from 70% to around 30%, and gas production ceased. Therefore on day 456 one liter of fresh carbon (10% of the total carbon bed volume) was added to avert reactor failure. Performance of the system in terms of COD, TOC, phenol, and cresol improved immediately, as shown in Figure 13. On day 461 a 10% increase in gas production was noted, but only for a short period of time. Within 10-12 days of carbon addition, the removal efficiencies of the process had declined to their previous unsatisfactory levels. On day 488, a second dose of carbon was added to the reactor by removing 3 L of spent carbon from the reactor and adding 2 L of fresh carbon; returning the carbon bed to its original volume of 10 L.

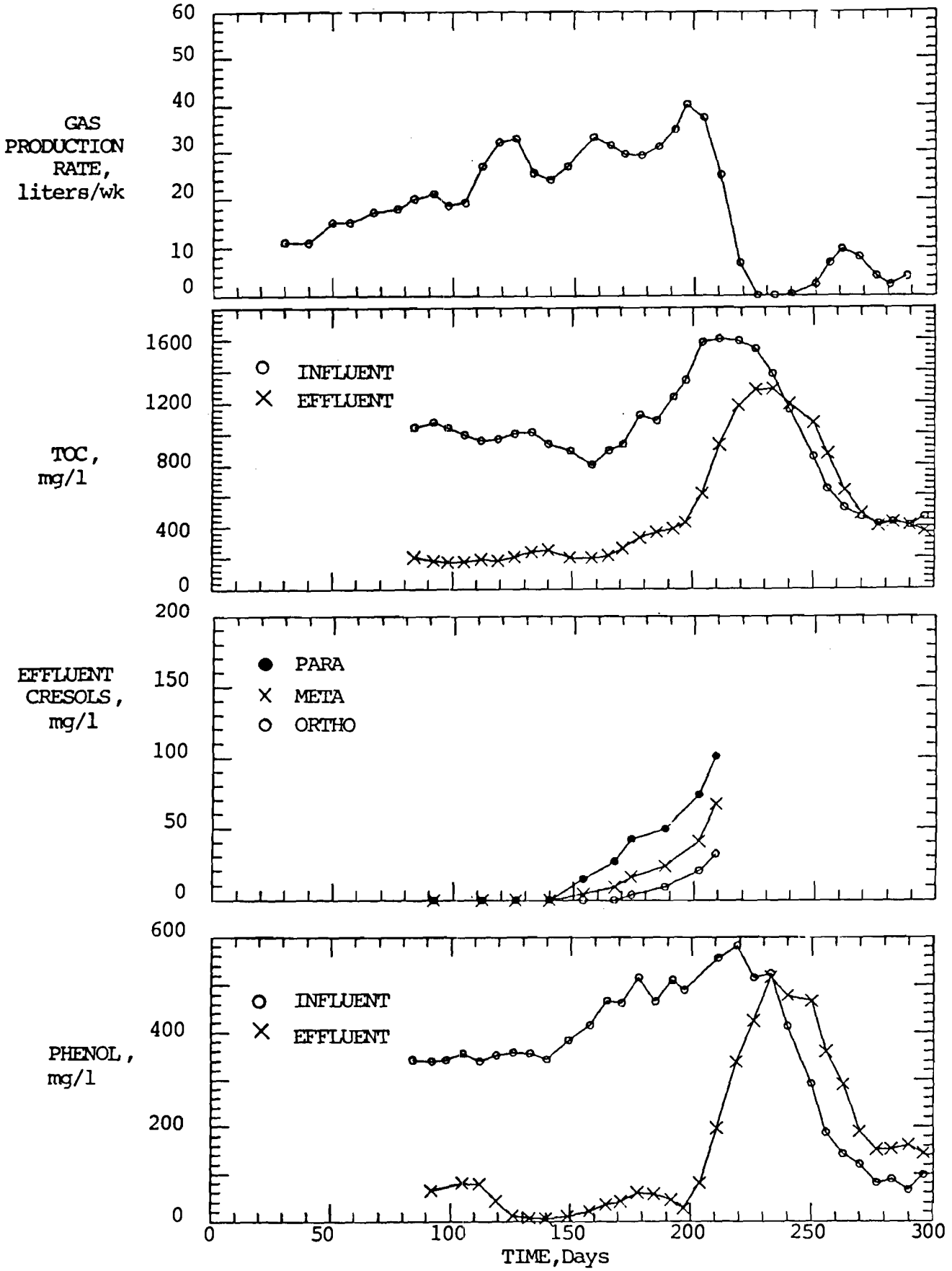

Fig. 11 Gas Production and Constituent Removal, System II.

Table 6. Organic Constituents Extracted from Granular Activated Carbon Removed from Inhibited Biological Reaction

Compound	Concentration mg/l
Pyridine	4.6
2-Picoline	3.7
4-Picoline	5.8
Aniline	1.9
Benzonitrile	0.7
2-Methoxyphenol	169.0
2,6-Dimethylphenol	6.8
2,4-Dimethylphenol 2,5-Dimethylphenol	125.0
4-Ethylphenol 3,5-Dimethylphenol	118.0
3-Ethylphenol	9.2
3,4-Dimethylphenol	28.6
3-Methoxyphenol	1.2
4-Methoxyphenol	1.0
2,3,5-Trimethylphenol	3.4
Indole	2.5

Table 7. Comparison of Ratio of Substituted Phenols to Phenol in Reactor Influent and Granular Activated Carbon Extracted After Reactor Failure

	Influent	Carbon Extract
o-cresol	0.11	2.74
m-cresol	0.17	9.12
p-cresol	0.16	
C_2-phenols	0.05	4.90

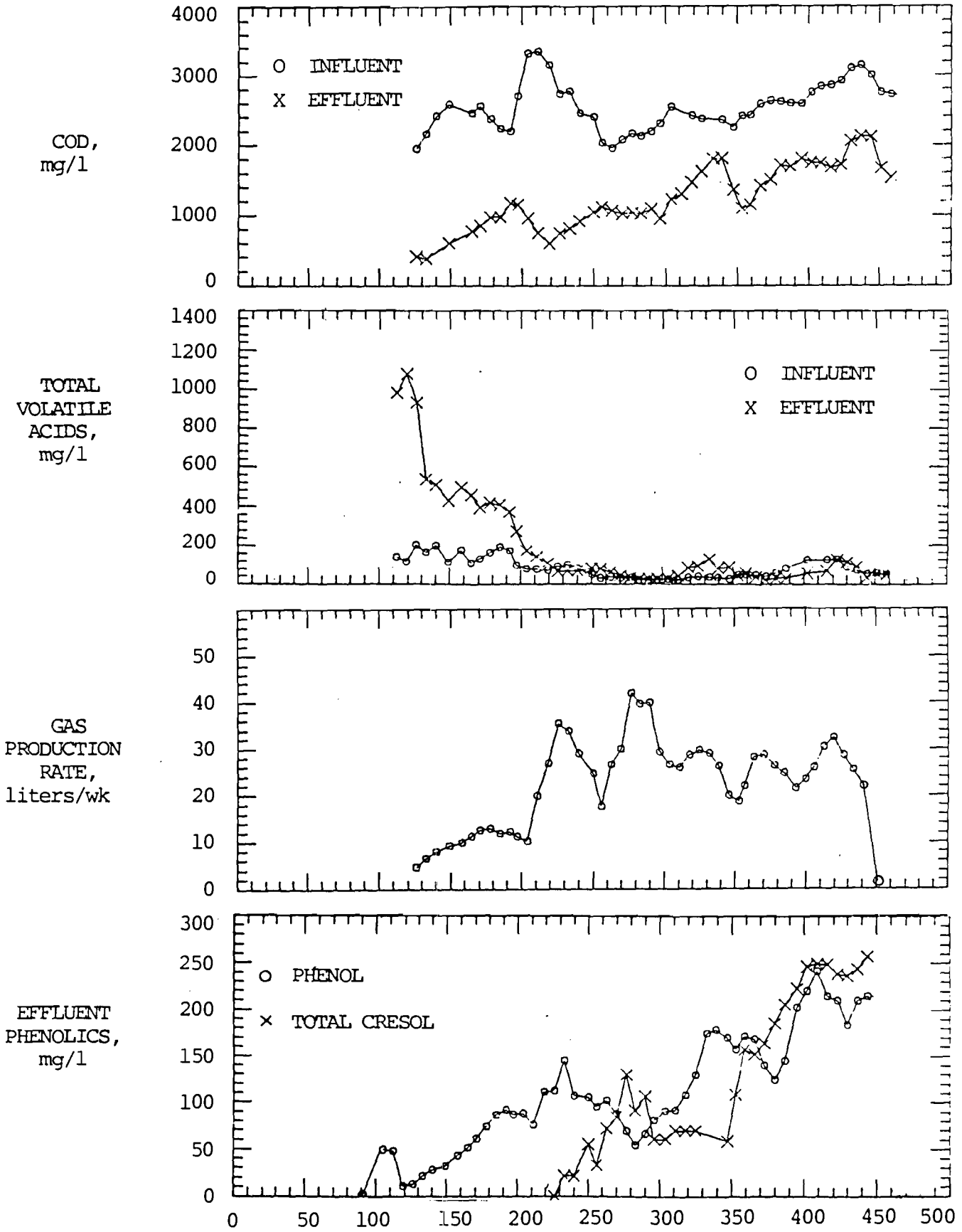

Fig. 12 Gas Production and Constituent Removal of System III Prior to Carbon Cycling.

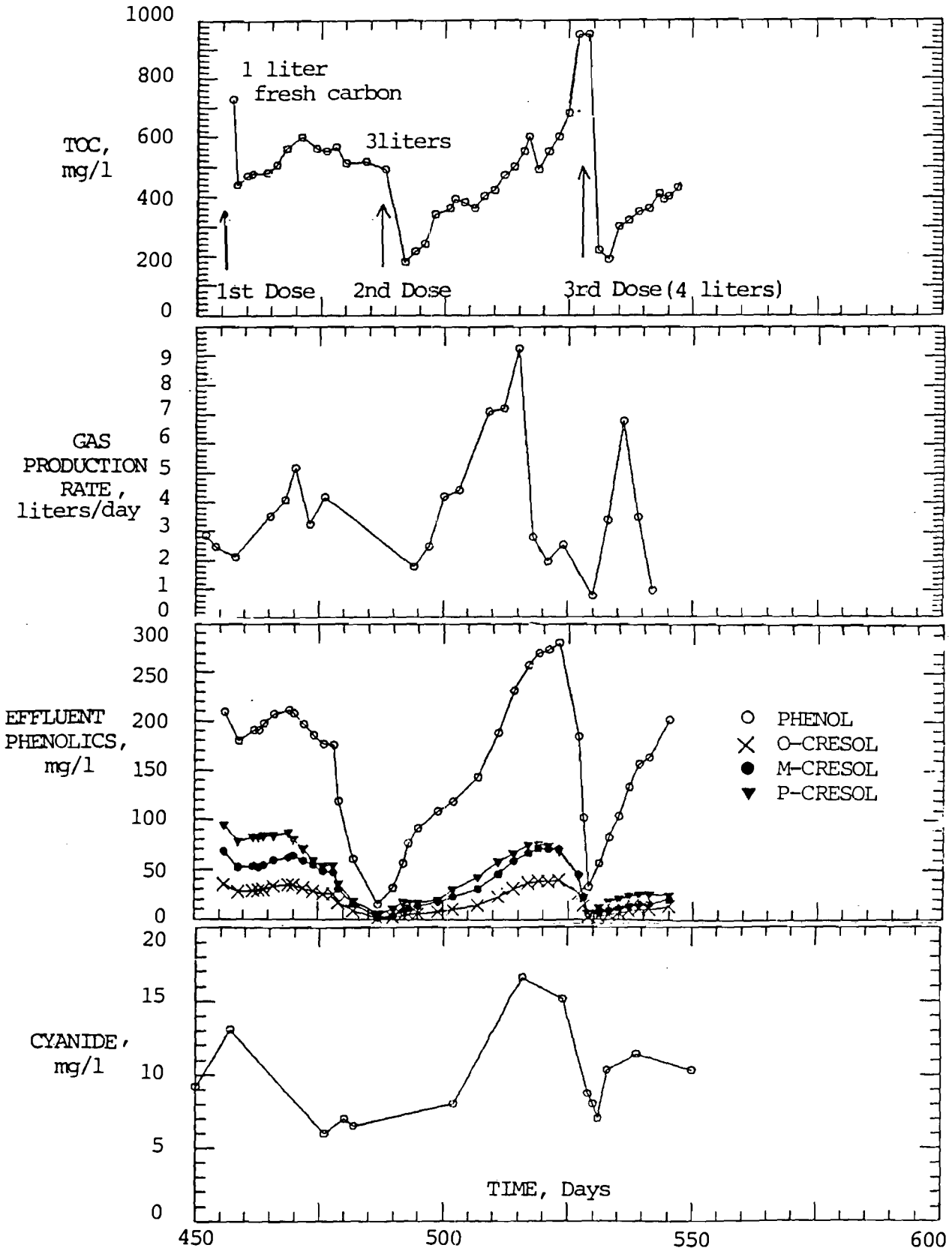

Fig. 13 Gas Production and Constituent Removal of System III During Carbon Cycling.

Removal efficiencies were again improved immediately, and were followed by a large increase in gas production to about 8.4 L per day (70% methane) or approximately the same volume of gas produced during peak performance of both systems II and III. This fact again seemed to point to the existence of an optimum biological growth condition just beyond initial cresol breakthrough but before total saturation (and the possible breakthrough of other organic and inorganic constituents). Additionally, since phenol breakthrough had previously occurred, its availability as a substrate for biological growth was at a maximum under this condition. The pragmatic implications of these observations become clear - if the reactor could be operated at biologically conducive conditions for the long term, maximal substrate use and minimum dilution could possibly be realized. The engineering considerations such as reactor design and operational strategies remain to be optimized. Economic feasibility will ultimately depend on these engineering considerations, and the advantages potentially available from efficient use of anaerobic over aerobic stabilization systems.

Moreover, the AFACF provides a degree of treatment beyond that available from activated sludge, since even at long retention times a number of pollutants which are adsorbed in AFACF escape aerobic conversion. Further, the removal of these same pollutants has been observed as being instrumental in determining the efficiency of nitrification and denitrification systems downstream as discussed later.

Series of AFACF Reactors - Carbon Scheduling

From the observed behavior of the AFACF and nitrification process in response to cyclic additions of fresh activated carbon, the necessity of maintaining active adsorption as an *in situ* pretreatment was evident. From an operational viewpoint, carbon replacement should occur as infrequently as possible to avoid downtime and minimize loss of biomass. Two immediate needs arise: a simple and effective method for the physical replacement of carbon, and an operating strategy including a carbon replacement schedule and analytical monitoring procedures.

Insofar as the replacement of carbon is concerned, one approach is a series of reactors representing a moving-bed type of system, wherein reactors are operated until carbon saturation and then temporarily removed from service for carbon bed regeneration and/or replacement. This approach was studied and results are illustrated in Figure 14, which shows that virtually no gas production was observed in the second column in the series (B) until phenol breakthrough occurred. At this point the gas production rate began to slowly increase concomitant with the rise in phenol concentration. The third column in the series did not produce any gas nor have any phenol in the effluent. The first reactor in the series would be removed as soon as the second reactor has attained a stable level of performance. Unfortunately, the second reactor's performance declined before substantial biological activity could be established. Perhaps the microorganisms did not have sufficient time to acclimate to the phenolic carbon sources before the onset of inhibition.

The other carbon replacement strategy studied involved the removal of a percentage of the spent carbon and addition of fresh carbon as previously illustrated in Figure 13. This method also works well, although it requires a greater carbon replacement frequency and more operator time than does the series-reactor approach. Additional plumbing is also required to recirculate

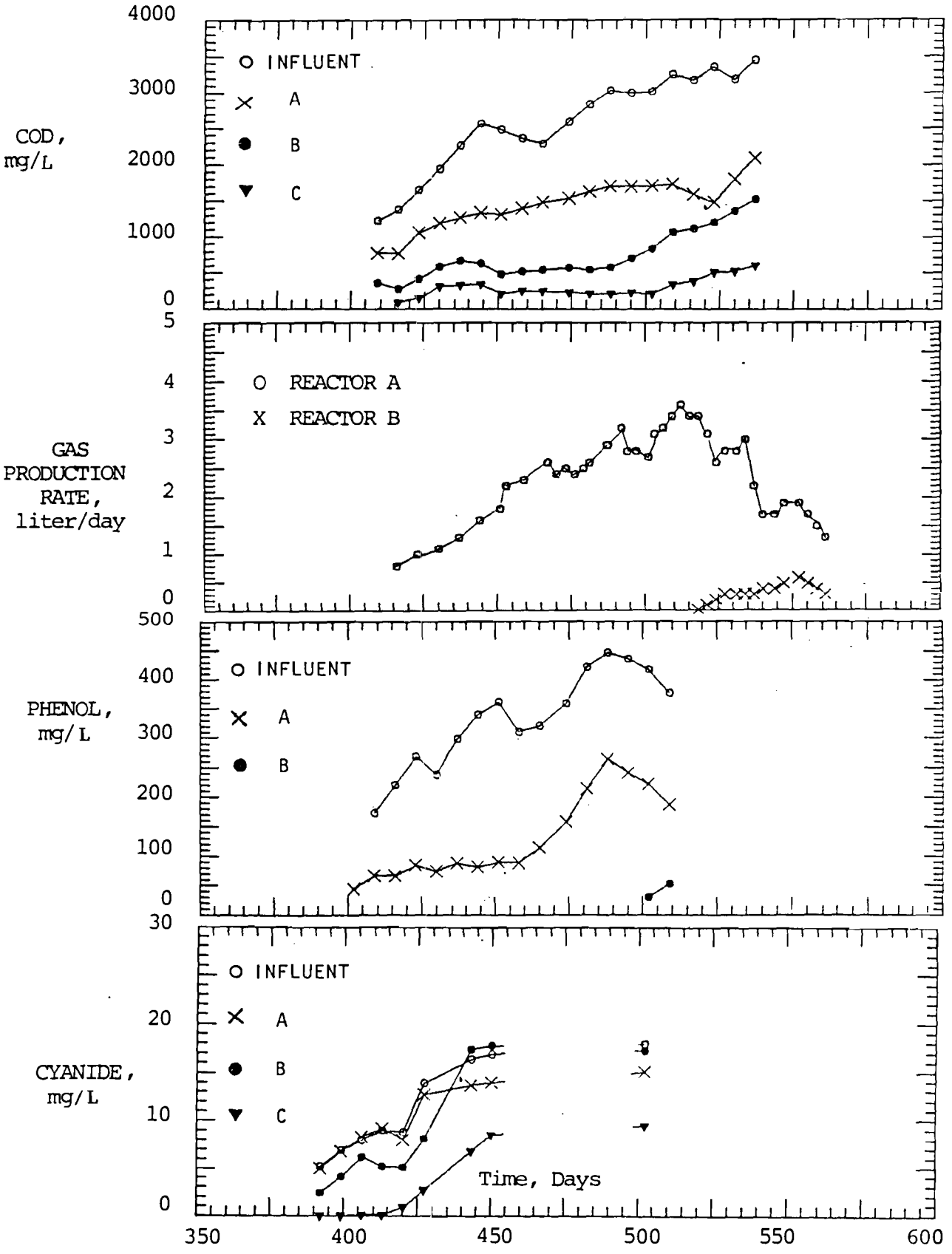

Fig. 14 Gas Production and Constituent Removal of Three Carbon Filters in Series - System IV.

process water through carbon addition and removal appurtenances in order to keep the bed anaerobic during replacement operations. This approach allows for a good deal of flexibility in process control and for rapid generation of operational data from which carbon replacement schedules can be established.

Adsorption Contribution to Wastewater Treatment

The relative contributions of adsorption and biodegradation to the overall TOC removal can be separated through a material balance on carbon as illustrated for system III in Table 8. Table 8 relates the performance of system III for the five months following the last glucose addition. For the period with no glucose in the feed, the table reflects an 80-90% contribution to total carbon (TC) removal by adsorption until biological activity increased around Day 270. During the ensuing two months of peak biological activity (Days 270-340), the adsorption contribution first decreased to 9%, then increased again to 75%, then decreased to zero on Days 334-340 where it appears that bioregeneration (defined as gaseous carbon production in excess of aqueous carbon input) may have occurred.

Biological Contribution to Adsorption

The production of biogas in excess of organic carbon in the influent, as witnessed on Days 334 and 340 (Table 8), possibly indicative of bioregeneration, may have served to increase the service life of the granular activated carbon. A comparison of the breakthrough curve produced for system III to a breakthrough curve generated in the absence of biological activity is shown in Figure 15. The nonbiological breakthrough curve was generated in a 1/2 in. internal diameter I.D. plexiglas column using ten g of 50 x 60 mesh carbon preceded by approximately 5 carbon bed depths of 35 mesh sand. The feed used was effluent which was taken from system III near carbon saturation, then refrigerated and monitored for phenol and cresol stability to assure bioinactivity. Influent phenol and total cresol concentrations were 150 and 190 mg/L, respectively.

The relationship between phenol and cresols for activated carbon (AC) and biological activated carbon (BAC) is illustrated by Figure 15, which shows that total cresol breakthrough for the biological carbon lags behind that of nonbiological carbon by about 200 g of carbon per kg of activated carbon used. This apparent increase in cresol capacity could have been due to bioregeneraton and/or desorption of phenol from the carbon to accommodate cresol adsorption. It can be seen from Figure 15 that phenol desorbed from both nonbiological system (AC) as well as the biological activated carbon (BAC) system. The rate of desorption of phenol appeared to be much greater in the BAC system, thus allowing for the better accommodation of cresols and other higher molecular weight organics. It is interesting to note that the area between the phenol curves for AC and BAC roughly corresponds to the area between cresol curves for AC and BAC in Figure 15.

Suggestion for Operation

The effects of adsorption on the cyanide concentration are also particularly interesting. A decrease in cyanide removal efficiency is observable just following cresol breakthrough during both normal operation and carbon cycling studies. At these times, the cyanide concentration reached nearly 20 mg/L, which may well be a principal cause of inhibition. Similar trends can be seen in the data of Suidan et al. in that on Days 40 to 60 and 140 to 210, the cyanide concentration rose to above 20 mg/L and the process

Table 8. Mass Balance[a] on Carbon in System III.

DATE	DAY	INFLUENT TOTAL CARBON, (mg/l)	INFLUENT INORGANIC CARBON, (mg/l)	EFFLUENT TOTAL CARBON, (mg/l)	EFFLUENT INORGANIC CARBON, (mg/l)	TOTAL CARBON REMOVED, (mg/l TC)	GASEOUS CARBON PRODUCED, (mg/l)	DISSOLVED GASEOUS CARBON (mg/l TIC)	ESTIMATED BIOMASS CARBON, (mg/l)*	ADSORBED CARBON, (mg/l)	REMOVED AS ADSORPTION, (%)	REMOVED AS BIOGAS, (%)
5/10	219	1370	160	720	190	650	55	30	10	555	85	13
5/17	226	1320	140	540	120	780	30	20	5	725	93	6
5/24	233	1070	150	660	200	410	60	50	10	290	71	27
5/31	240	1040	220	620	240	420	35	20	5	360	86	13
6/10	250	1040	160	580	160	460	80	0	10	370	80	17
6/16	256	940	140	680	190	260	40	50	10	160	62	35
6/24	264	940	160	670	180	270	35	20	5	210	78	20
7/01	271	970	180	620	180	350	245	0	25	80	23	70
7/08	278	920	180	520	140	450	255	-40	20	215	48	48
7/14	284	960	150	620	220	340	205	70	25	40	12	81
7/21	291	1000	125	660	190	340	215	65	30	30	9	82
7/27	297	1080	140	820	160	260	170	20	20	40	15	73
8/04	305	1060	200	660	190	400	180	-10	15	215	54	42
8/11	312	1090	180	550	180	540	135	0	15	390	72	25
8/18	319	1020	180	420	125	600	190	-55	15	450	75	22
8/25	326	1060	150	680	190	380	240	40	30	70	22	74
9/02	334	1100	190	1020	180	80	200	-10	20	-130	0	100
9/08	340	1140	240	1040	240	100	120	0	10	-30	0	100
9/16	348	1160	200	640	190	520	125	-10	10	385	74	22
9/22	354	1040	120	600	180	400	120	60	20	200	50	45
9/28	360	1060	130	600	170	460	70	40	10	340	74	24

*Estimated as approximately 10% of gaseous carbon produced.

[a]Total Carbon Removed = Gaseous Carbon Produced + Dissolved Gaseous Carbon + Estimated Biomass Carbon + Adsorbed Carbon.

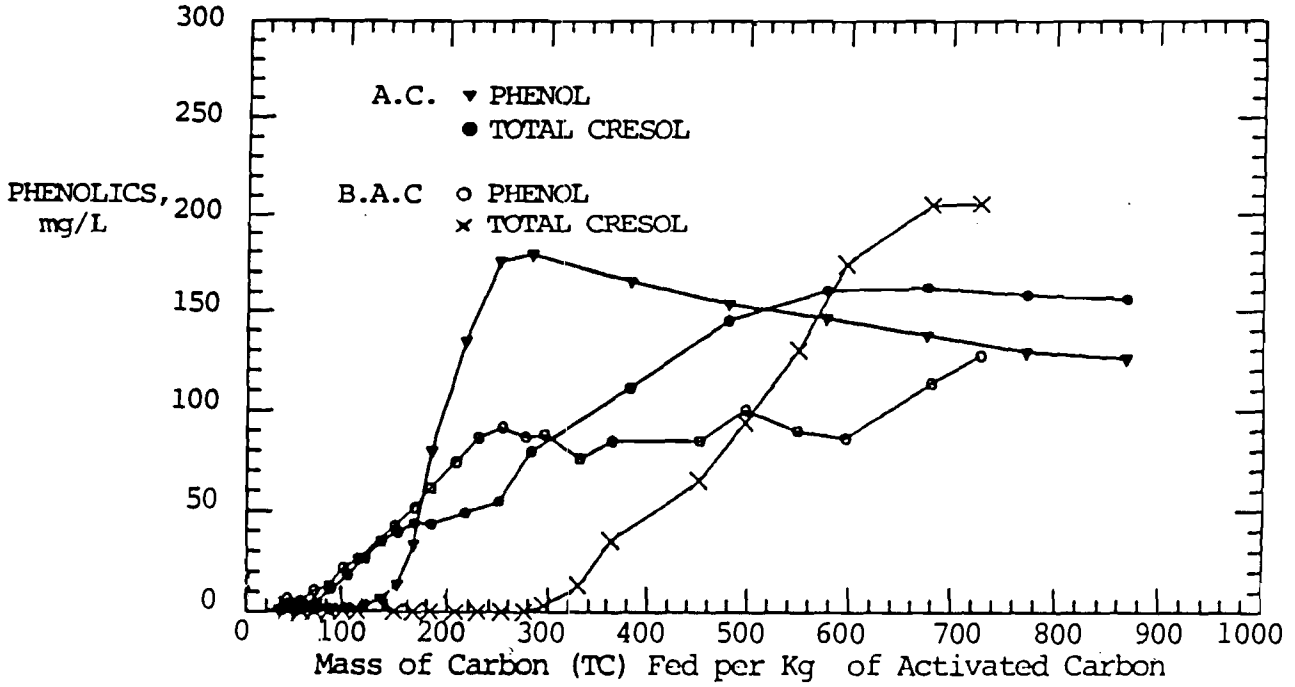

Fig. 15 Comparison of Biological Activated Carbon (BAC) and Non-Biological Activated Carbon (AC) Phenol and Total Cresol Breakthrough Curves

exhibited inhibitory behavior as reflected by decreases in COD and DOC removals[22].

Discernment of the true identity of the inhibitory agent(s) would be of great benefit in optimizing biological process performance; however, it is not entirely necessary for process control. Correlations between process efficiency and monitoring parameters such as cresol, cyanide, gas production, and COD can be used as indicators of carbon saturation and biological activity and therefore serve as key control parameters. Recognition of an accumulation of adsorbable and/or inhibitory constituents in the bulk solution could indicate the need for carbon replacement in advance of biological failure and help maintain optimum operating conditions.

From experiences with 10% dilutions of wastewater, approximately 1.2-1.6 kg of activated carbon were required per kg of carbon fed before total inhibition occurred. At loading rates of 15 g of carbon/day this corresponded to around 50 days of operation per kg of activated carbon. Carbon cycling studies indicated a slightly higher frequency of carbon replacement is necessary to assure a high biological conversion rate; around 25 days of operation per kg of activated carbon seem optimum.

For carbon cycling operations, removal of around 25% of the bed volume does not seem to severely affect conversion; however, removal of a larger amount may necessitate a reacclimation period due to excessive biomass removal. For the series reactor approach, reactor size will ultimately be determined by the safety level desired in terms of biological activity overlap between sequential reactors and the degree of effluent polishing desired by adsorption.

Carbon cycling studies and series-reactor data have been combined with initial operational data on three separate reactor systems to suggest carbon replacement frequencies necessary for optimum biological-adsorptive process performances. A carbon replacement frequency of approximately 0.6-0.8 kg AC per kg of carbon fed (25 days/kg AC) seems biologically optimal. For a removal/replacement approach, no more than 25% of the bed volume should be removed at a time in order to avoid excessive loss of biomass.

NITRIFICATION STUDY

In order to remove ammonia nitrogen from the wastewater after TOC removal was accomplished in the anaerobic filter, the anaerobic filter effluent was treated using a single stage activated sludge nitrification system. In this type of biological waste treatment system, microorganisms are encouraged to grow utilizing ammonia-nitrogen as a substrate and converting it to nitrate nitrogen according to the following equation, $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$. This process occurs when there is a limited amount of TOC available for the microorganisms to use as a substrate. In addition since the processes produces hydrogen ion, sufficient alkalinity must be supplied in order to maintain the pH at a relatively constant value. This was done by the addition of $NaHCO_3$ to the influent.

The nitrification experiments lasted 367 days and can be divided into five phases as follows:

- Acclimation Phase - when a nitrifying activated sludge was slowly acclimated to feed on the anaerobic effluent.
- Pseudo-Steady-State Phase - operation during which ammonia removal and other operation parameters remained relatively constant.
- Inhibition Phase - period during which poor performance by the anaerobic fluidized activated carbon filters in removing TOC and other constituents resulted in poor performance of the nitrification system.
- Powder Carbon Phase - during which powdered activated carbon (PAC) was added directly to the nitrification system to overcome the inhibition.
- Carbon Cycling Phase - during which a portion of the granular activated carbon was periodically replaced in the anaerobic fluidized activated carbon filters in order to improve their performance and prevent inhibition of the nitrification system.

The performance period for each phase of the nitrification study is shown in Table 9. Note that from Days 132 through 160, the nitrification system was short of feed several times; therefore samples were not routinely obtained and no data were reported.

Acclimation Phase. During Phase 1 of the study (Days 1 to 56), a nitrifying activated sludge obtained from a local pure oxygen wastewater treatment plant (South Cobb Plant, Austell, GA) was gradually acclimated to the anaerobic filter effluent which contained approximately 600 mg Total Kjeldahl Nitrogen (TKN)/L (527 mg NH_3-N/L). In the acclimation procedure (Table 9), the feed concentration (of the anaerobic filter effluent to the nitrification system) was increased in five steps from 10% to 100% anaerobic effluent. Each step increase in feed concentration during the acclimation phase lasted from 8 to 13 days.

Table 9. Phases of Nitrification Experiments.

PHASES OF NITRIFICATION EXPERIMENTS

Phase 1	Acclimation	Day	0 - 56
Phase 2	Pseudo-steady state operation		57 - 132
Phase 3	Inhibition		160 - 203
Phase 4	Addition of PAC to aeration tank		204 - 249
Phase 5	Replacement of GAC in anaerobic filter		250 - 367

No data available during day 133 - 159

Throughout the acclimation phase, the hydraulic retention time (HRT) was maintained at 18 hours and the solids retention time (SRT) was maintained at 22 days beginning with Period 1c (Table 10). Loadings were gradually increased from 0.06 to 0.23 kg NH_3-N/kg MLVSS·day and from 0.09 to 0.43 kg COD/kg MLVSS·day by increasing the concentration of anaerobic effluent fed to the system. Figure 16a (Days 1 to 56) indicates that effluent NH_3-N level occasionally increased suddenly at the beginning of each step but after 2 to 3 days, it decreased rapidly to its original level again. However, in other cases, there were no changes in final effluent ammonia from one step to another, indicating that the activated sludge could quickly acclimate to the feed change.

Table 10 also shows that during the acclimation phase as much as 99% of the NH_3-N was removed; effluent NH_3-N was less than 2 mg/L and almost all NH_3-N was converted to NO_3^--N. During the acclimation phase, COD and TOC removal increased from 40% initially to 80% at the end of the test period. Aeration basin MLSS increased from 1560 mg/L to 3170 mg/L during this same period.

Pseudo-Steady-State Operation. After acclimation, pseudo-steady-state operation of the nitrification system was attained. The system was first operated at the HRT and SRT used in the acclimation phase, (18 hours and 22 days, respectively). Data obtained during Period 2a (Days 57 to 82) showed that, although effluent COD and TOC were relatively constant (206 mg/L and 127 mg/L, respectively, Figure 16b), effluent NH_3-N gradually increased from 2 mg/L to 46 mg/L (Figure 16a) and effluent NO_2^--N increased as well (Figure 16c, Days 48 to 76). This indicated some inhibition of the nitrification process under these operating conditions. The SRT was increased from 22 to 31 days and the HRT from 18 to 30 hours; correspondingly, NH_3-N loading decreased from 0.27 to 0.15 kg NH_3-N/kg MLVSS·day and COD loading from 0.52 to 0.35 kg COD/kg MLVSS·day. Figures 16a and 16b (Period 2b, Days 83 to 132), indicate that, under these new operating conditions, the effluent quality from the nitrification system was very stable although influent COD and TOC continuously increased. However, a peak of approximately 125 mg NO_2^--N/L occurred in the last several days of Period 2b (Figure 16c, Days 123 to 132). Based on the data in parentheses in Table 10, TKN removal during this period was as high as 97% with effluent TKN of 18 mg/L. The effluent NH_3-N was only 4.4 mg/L, whereas effluent NO_3^--N was 485 mg/L. The corresponding COD and TOC removals were 95% and 91%, respectively. These data indicated that nitrification was relatively complete and organic matter reduction was high.

As shown in Table 11, a nitrogen balance was performed for a 30-day span during Period 2b (Days 97 to 127). The average effluent TKN, NO_3^--N and NO_2^--N accounted for 3%, 83.7% and 3.5% of the influent TKN, respectively. The total effluent nitrogen was 90.2% of the influent TKN or only 9.8% of the influent TKN was unaccounted for (the percentage of unaccounted nitrogen varying from 1.0% to 18.1%). This unaccounted portion of influent TKN was attributed to microbial cell growth, possible denitrification, air stripping, and analytical error.

The production of sludge was estimated during the same period. On the average, the sludge growth rate was 1.2 g/day and COD removed was 9.5 g/day. The computed yield coefficient was 0.13 kg sludge formed/kg COD removed, which

Table 10. Operating conditions and performance of nitrification system

Phase	Duration (days)	Period	Time (day)	Duration (days)	Dilution Ratio	SRT (days)	HRT (hrs)	NH_3-N loading	COD loading
1	56	1-a	1-13	13	1:9		18	0.06	0.09
		1-b	14-23	10	1:3		18	0.09	0.14
		1-c	24-31	8	1:1	22	18	0.15	0.14
		1-d	32-44	13	1:0.33	22	18	0.18	0.28
		1-e	45-56	12	1:0	22	18	0.23	0.43
2	76	2-a	57-82	26	1:0	22	18	0.27	0.52
		2-b	83-132	50	1:0	31	30	0.15	0.35
3	44		160-203	44	1:0	26→40	25→33	0.17→0.13	0.43→0.33
4	46	4-a	204-218	15	1:0	31	30	0.20	0.61
		4-b	219-249	31	1:1	31	43	0.08	0.24
5	118	5-a	250-277	28	1:1	30	30	0.08	0.20
		5-b(1)	278-303	26	1:0	30	18	0.18	0.24
		5-b(2)	304-325	22	1:0	30	30	0.15	0.40
		5-c	326-367	42	1:0	30	30	0.15	0.36

Phase: 1. Acclimation; 2. Pseudo-steady state operation; 3. Inhibition; 4. Addition Of powdered activated carbon to aeration basin; 5. Periodical replacement of granular activated carbon in anaerobic filter.

Dilution ratio: Ratio of parts of anaerobic effluent to parts of tap water.

Unit of NH_3-N loading: kgNH_3-N/kgMLVSS/day.

Unit of COD loading: kgCOD/kgMLVSS/day.

Period	TOC(mg/l) Inf	Eff	Rem%	COD(mg/l) Inf	Eff	Rem%	NH_3-N(mg/l) Inf	Eff	Eff NO_2^--N mg/l	Eff NO_3^--N mg/l	MLSS mg/l	Alkalinity consumption
1-a	48	28	42	99	60	39	65	0.8		56	1563	5.6
1-b	110	30	73	182	48	74	111	0.4	0.3	101	1902	5.7
1-c	227	46	80	256	91	64	263	1.8	2.4	221	2655	6.0
1-d	466	56	88	613	91	85	397	1.6	0.3	369	3294	6.1
1-e	692	131	81	895	196	78	485	2.1	10	419	3167	5.6
2-a	594	125	79	894	210	77	473	23	64	341	2509	5.5
2-b	776	72	91	1286	189	85	527 (TKN601)	4.4 (TKN18.3)	16	485	3238	5.8
3				1364	455	67	543	30→520	85	466→18	3318	
4-a				1711	398	77	568	414	24	16	2715	
4-b				955	204	79	294	208→1.8	12	25→295	2451	
5-a				682	84	88	260	1.9	0.3	194	2911	5.9
5-b(1)				680	92	86	515	3.7	0.5	476	4188	6.7
5-b(2)				1810	369	80	682	142→3.0	384→0.7	346→700	4153	
5-c				1393	184	87	579	7.0	4.2	597	3411	7.2

Unit of alkalinity consumption: mg Alkalinity consumed/mg NH_3-N removed

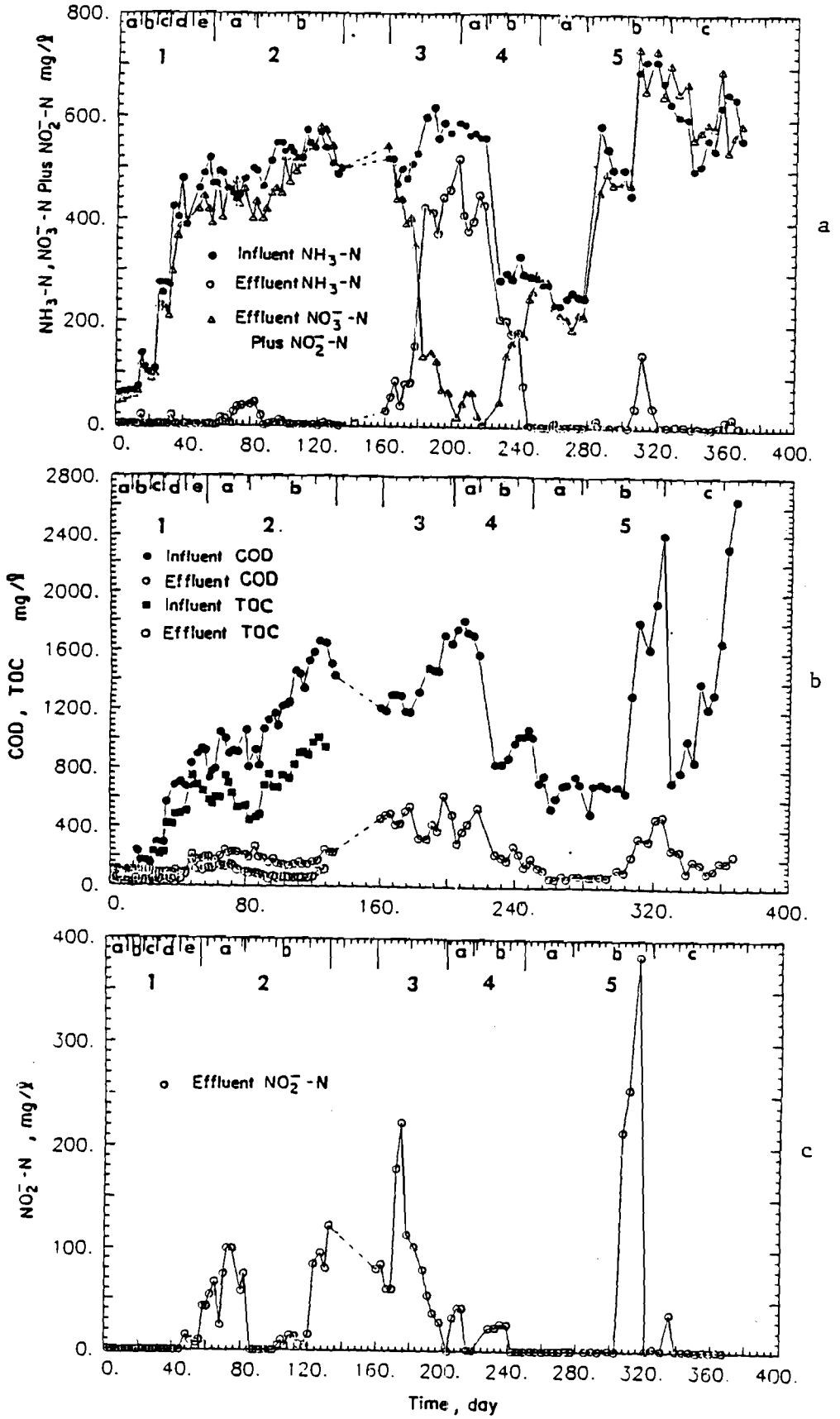

Fig. 16 Nitrification System NH_3-N, NO_3^--N, NO_2^--N, COD, TOC Concentrations

Table 11. Nitrogen Balance Data (Day 97-127)
For Nitrification System.

Day	Inf.	Eff.				Total N not accounted for	
	ΣN_{inf}=TKN	TKN	NO_2^--N	NO_3^--N	ΣN_{eff}*	$\Sigma N_{inf}-\Sigma N_{eff}$	%
97	580	24.5	0.7	450	475	105	18.1
99	555	20.9	0.4	520	541	14	2.5
102	580	15.0	5.0	468	488	92	15.9
104	595	15.5	10.2	512	538	57	9.6
106	590	14.0	3.9	490	508	82	13.9
109	595	14.2	14.7	494	523	72	12.1
112	625	19.5	14.1	524	557	68	10.9
114	615	16.2	5.9	536	558	57	9.3
117	635	15.8	4.6	536	556	79	12.4
120	635	13.6	16.0	564	594	41	6.5
123	635	23.5	85.0	490	598	37	5.8
127	575	27.2	96.0	446	569	6	1.0
Ave.	601	18.3	21.4	503	542	59	9.8
% of Inf TKN	100	3.0	3.5	83.7	90.2	9.8	

All values are in mg/L except for percentages.

*ΣN_{eff}=TKN + NO_2^--N + NO_3^--N

was consistent with data obtained by Olthef[10] for coke oven wastewater treatment. Calculated alkalinity consumption for the same period was 5.8 mg alkalinity consumed/mg NH_3-N removed.

Inhibition of Nitrification. The anaerobic filter effluent quality began to deteriorate from saturation of the activated carbon in the filter with refractory compounds such as cresols after 10 months of operation. The effluent COD eventually increased to 2100 mg/L with only 30% COD removal. Correspondingly, effluent phenol from the anaerobic filter increased to 270 mg/L with only 50% phenol removal and effluent total cresols increased to 230 mg/L without any evidence of cresol removal. That the poorer quality of anaerobic effluent resulted in inhibition of the nitrification process can be seen from Figure 16a where from Day 160 the performance of the nitrification system began to deteriorate. By Day 203 the system was almost completely inhibited and effluent NH_3-N was as high as 520 mg/L and effluent NO_3^--N plus NO_2^--N as low as 18 mg/L. Although the SRT and HRT were increased to 40 days and 33 hours, respectively, and an automatic pH controller was installed in the aeration basin to maintain pH between 7.0 and 7.5, the system performance did not improve.

As shown in Table 9, the loadings to the nitrification system during the inhibition period (Phase 3) were maintained at 0.17 to 0.13 kg NH_3-N/kg MLVSS·day and 0.43 to 0.33 kg MLVSS·day, comparable to those during pseudo-steady-state operation (Phase 2). Other operating parameters such as pH, alkalinity, and DO were also normal. The inhibition of the nitrification system might, therefore, have been attributable to the presence of some inhibitory compounds in the influent of the nitrification system; the most likely candidates were CN^-, SCN^-, S^{-2}, phenol, cresols, and other trace organic compounds in the coal gasification wastewater. However, analytical determinations indicated that the influent concentrations of CN^-, SCN^- and S^{-2} in the nitrification system were within the range of 3 to 17 mg/L, 4 to 20 mg/L, and 2 to 5 mg/L, respectively. Results reported in the literature[4-6, 22, 24-27] indicate no inhibition to nitrifying organisms attributable to these compounds at these concentrations.

Similarly, phenol in the influent to the nitrification system varied from 53 mg/L to 409 mg/L, and in most cases could be removed completely in the system as shown in Figure 17a. As indicated by several investigators[4, 24, 26] phenol concentrations much higher than 400 mg/L could be removed entirely in the activated sludge process. Therefore, the inhibition of the nitrification system was not attributed to the presence of phenol.

Tomlinson, et al.[28] reported that nitrification (using activated sludge as a source of nitrifying bacteria) was inhibited by 12.8 mg/L o-cresol, 11.4 mg/L m-cresol, and 16.5 mg/L p-cresol. Suidan et al.[22] showed that 7.8 mg/L o-cresol and 12.1 mg/L m-cresol and p-cresol could be removed completely without causing any inhibition. This may have been the result of a difference in the acclimated activated sludge. In this study, in all cases influent o-cresol concentrations from 3 to 46 mg/L were readily removed in the nitrification system (Figure 17b). However, only 80% of m-cresol and p-cresol was removed during the inhibition phase (Days 160 to 218); 20 to 35 mg/L remained in the effluent (Figure 17c). This level of m-cresol and p-cresol concentrations were implicated as a cause of nitrification inhibition although they could not be specifically identified as the sole inhibiting compounds.

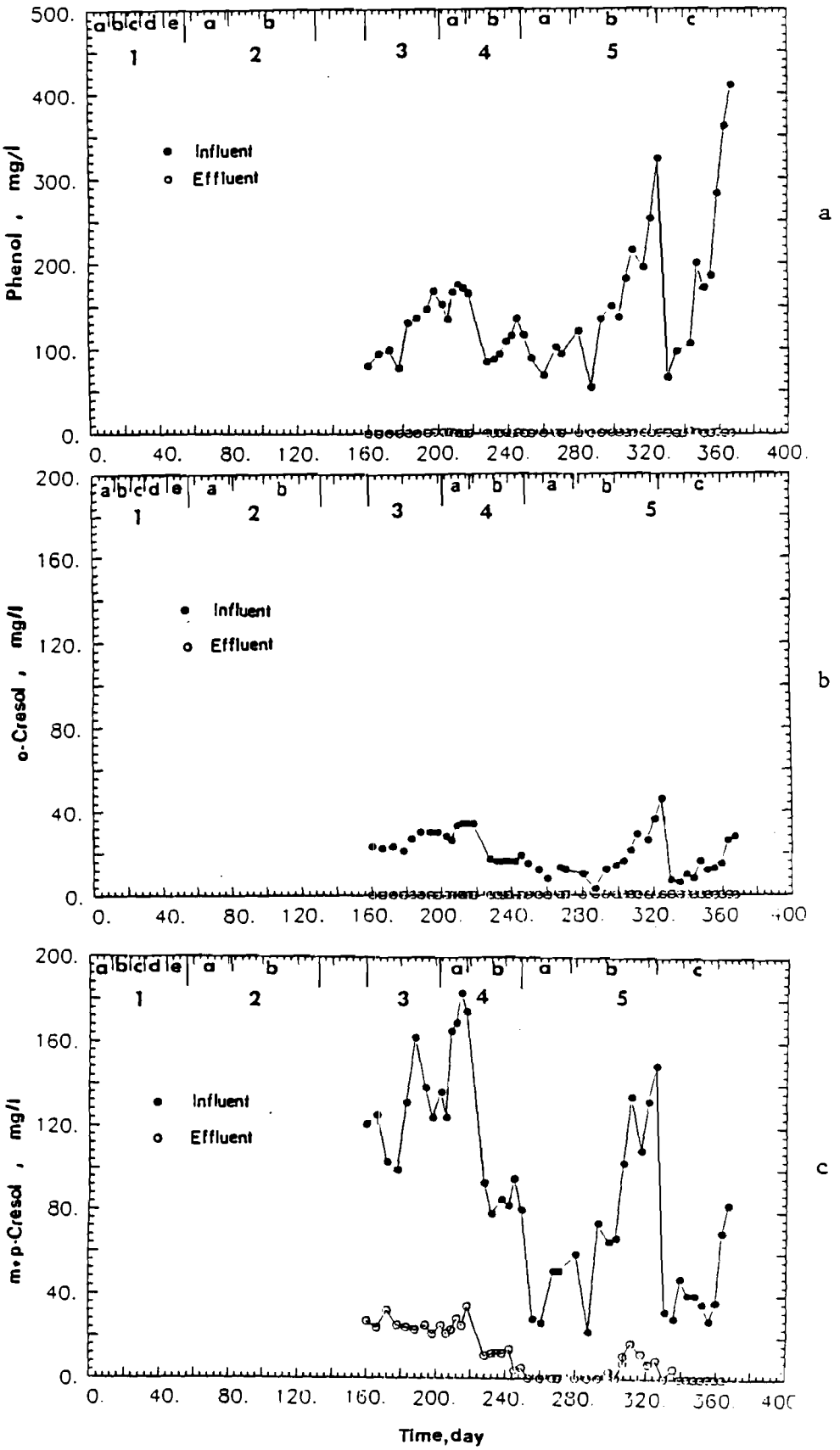

Fig. 17 Nitrification System Phenol, Cresol Concentrations

Because of the complex composition of the coal gasification wastewater, results shown in Figure 16a and Figure 16c (Days 244 to 304, and 321 to 367) indicated that when the total concentration of m-cresol and p-cresol in the nitrification effluent was less than 5 mg/L, the system performed very well with complete NH_3-N removal. However, when the effluent concentrations were higher than 15 mg/L (Figure 17c, Days 160 to 220 and 311), the system showed signs of inhibition (Figure 16a) with corresponding increases in effluent NH_3-N.

In general, there are two types of microorganisms that exist simultaneously in the activated sludge of a single-stage nitrification process. One is the autotrophic nitrifiers that convert NH_3-N to NO_2^--N and NO_3^--N and are extremely sensitive to inhibitory compounds. The other is the heterotrophic microorganisms responsible for removal of organic compounds. In this study, the ratios of COD to NH_3-N normally ranged from two to four and the heterotrophs accounted for a substantial fraction of microorganisms in the activated sludge[29]. Therefore, phenol and o-cresol in all cases, and m-cresol and p-cresol in most cases could be completely removed by the heterotrophs; effluent concentrations were below detection limits. The autotrophs were not inhibited and complete nitrification occurred. However, if influent m-cresol and p-cresol were more than, for example, 150 mg/L, although 80% of m-cresol and p-cresol could be removed by the heterotrophs, the remaining 30 mg/L of m-cresol and p-cresol in the aeration basin could inhibit the autotrophs and lead to nitrification inhibition.

Recovery of Nitrification from Inhibition. Addition of powdered activated carbon (PAC) improves the performance of nitrification by partial or complete removal of inhibitory compounds[30-33]. PAC was added to the nitrification system to restore the system to its original operating efficiency. During Phase 4 of the study, the initial carbon equilibrium concentration was 2500 mg/L in the aeration basin. A daily dose of PAC was added to supplement the loss of PAC from withdrawal of PAC-activated sludge mixed liquor to maintain the SRT. The dose corresponded to 100 mg/L of PAC added to the influent of the nitrification system. At a 31-day SRT and a 30-hour HRT, there was no apparent improvement in the nitrification system. Average effluent NH_3-N was 414 mg/L, and NO_3^--N plus NO_2^--N totalled 40 mg/L (Figure 16a, Period 4a, Days 204 to 218). The PAC concentration, with respect to the influent was, therefore, increased to 150 mg/L by decreasing the influent flow rate to two-thirds of its original value. At the same time, the influent was diluted one-to-one with tap water to expedite the recovery of the system from inhibition. As shown in Figure 16a and Figure 16c (Period 4b, Days 129 to 249) under the new SRT of 31 days and HRT of 43 hours, the nitrification system recovered very rapidly. NH_3-N in the effluent decreased from 208 mg/L to 3 mg/L, effluent NO_3^--N increased to 250 mg/L (Figure 16a), and effluent NO_2^--N decreased to 0.3 mg/L (Figure 16c).

In the meantime, a portion of the granular activated carbon (GAC) was periodically replaced to improve the performance of the anaerobic filter beginning on Day 250. At that time, PAC addition was discontinued. The system was operated at a one-to-one dilution until Day 278, at which time the system began receiving undiluted anaerobic filter effluent. As can be seen from Figure 16b, 17a, 17b and 17c (Phase 5, Days 250 to 367), each time a portion of the GAC in the anaerobic filter was replaced (Days 250, 278, and 326), the anaerobic effluent quality improved significantly. For instance,

COD, phenol, and cresols were reduced markedly, but over time their concentrations increased rapidly again. Although influent NH_3-N was relatively stable throughout each carbon replacement in the anaerobic filter, influent COD, phenol, and cresol varied significantly from the beginning to the end of each replacement period. However, the salient feature appeared during Phase 5 when the influent m-cresol and p-cresol in the nitrification system were much lower than during inhibition Phase 3a (except for Days 307 to 321 during which period a sudden increase in feed concentrations caused temporary nitrification inhibition, when effluent NH_3-N increased and effluent m-cresol and p-cresol concentrations exceeded 15 mg/L). Therefore, during Phase 5 the nitrification system performed well and the effluent NH_3-N remained very low (Figure 16a, Days 250 to 367).

Table 9 shows that during Periods 5b[1], 5b[2], and 5c (except Days 307 to 321) with undiluted anaerobic effluent used as feed, the nitrification system was operated at an SRT of 30 days, NH_3-N loading of 0.15 to 0.18 kg NH_3-N/kg MLVSS·day, and COD loading of 0.24 to 0.40 kg COD/kg MLVSS·day, similar to the operating conditions during the pseudo-steady-state operation Period 2b. System performance was excellent during Periods 5b and 5c; NH_3-N removal (99%) and COD removal (86%) matched those obtained in Period 2b.

A second nitrification system with the same configuration as the first, and seeded with activated sludge from the first nitrification system obtained during the inhibition period, was started and received effluent from a new anaerobic activated carbon filter system on Day 206. Because most of the organic compounds, including cresols, were removed by the newly installed anaerobic filter, the second nitrification system recovered completely in only 12 days and was continuously operated for 150 days with no sign of inhibition caused by organic compounds as shown in Figure 18. From Figure 18 it can also be seen that there were several peaks in effluent NH_3-N concentration, in most cases resulting from pH less than 6.5, and in the last case also from low DO (0.4 mg/L). After adjustment of pH and DO in the aeration basin, the effluent NH_3-N was reduced rapidly to its original concentration of less than 5 mg/L.

Solids Retention Time. As is well known, the nitrification process is characterized by the fact that the growth of autotrophic nitrifying organisms is very much slower than that of heterotrophs and the reaction rate of nitrification is correspondingly slower. This means that to maintain a population of nitrifiers, the SRT must be long enough to avoid "wash out" of nitrifying organisms from the system. The published research on nitrification of wastewater containing high concentrations of ammonia, was conducted with an SRT of 20 days or more and an NH_3-N loading of 0.01 to 0.5 kg NH_3-N/kg MLVSS·day. In this study the SRT was 22 days and 31 days and the NH_3-N loading was 0.27 and 0.15 kg NH_3-N/kg MLVSS·day. This is consistent with the data cited above. In general, the performance of the nitrification system seemed to become better and more stable under the conditions of longer SRT and lower NH_3-N loading.

NO_2^--N Accumulation. Incomplete nitrification occurred in some studies[27,30,33,34] and ammonia was mainly oxidized to nitrite rather than nitrate, which lead to NO_2^--N accumulations. In this study NO_2^--N accumulation occurred in certain cases. Figures 16a, and 16c indicate that NO_2^--N gradually increased during Period 2b (Days 83 to 132) without an increase in effluent NH_3-N. Otherwise, NO_2^--N accumulation always occurred

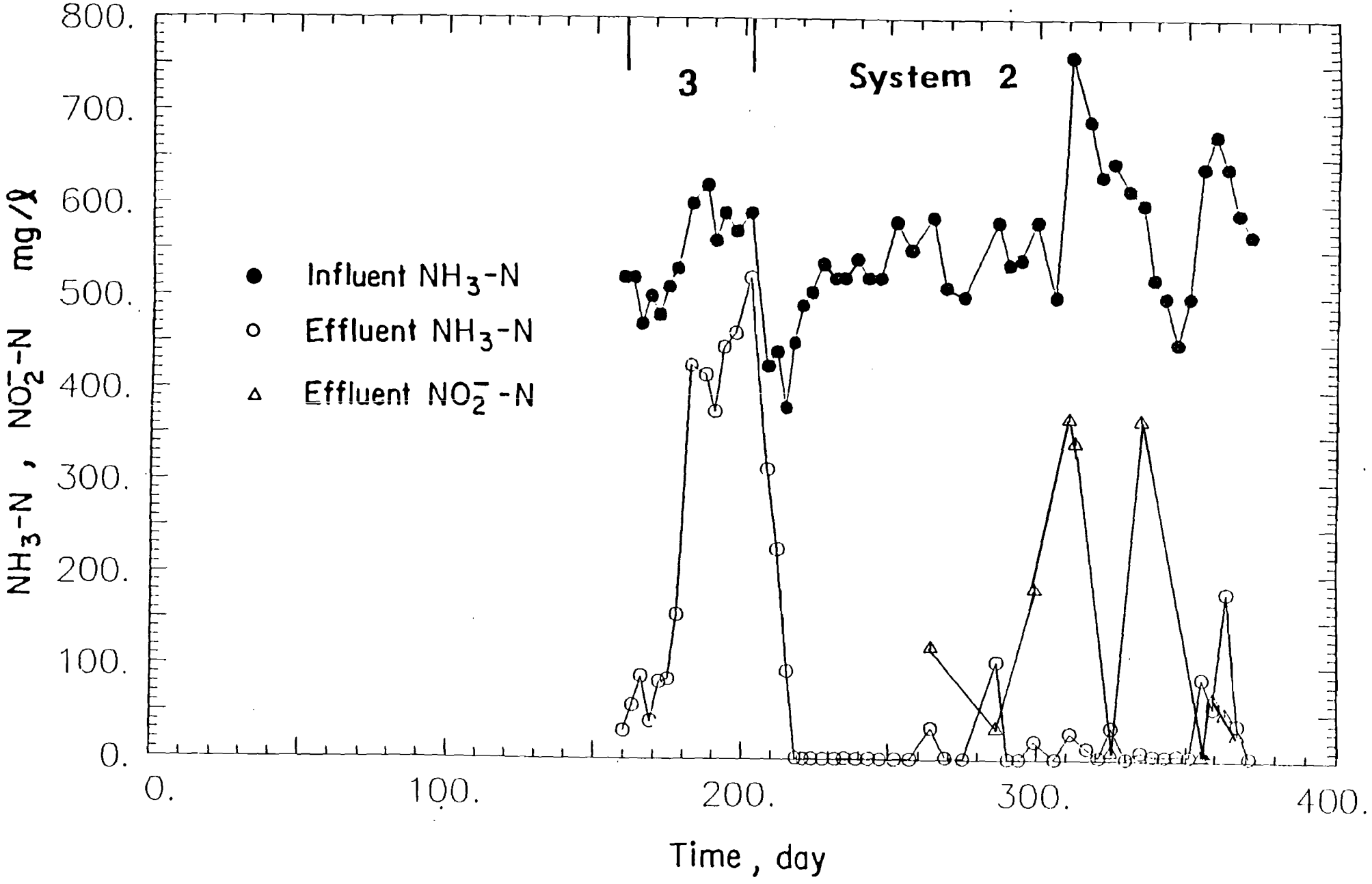

Fig. 18 Ammonia Removal and NO_2^--N Accumulation in the Second Nitrification System

with an increase of effluent NH_3-N during partial inhibition of nitrification (Days 57 to 82, 160 to 184, 307 to 321). Furthermore, pH control is a very important operating parameter for nitrification of high strength ammonia wastewaters. The aeration basin pH sometimes dropped to less than 6.5 because of insufficient supplementary alkalinity in the feed and resulted in temporary increases in effluent NO_2^--N as shown in Figure 18. However, as long as the pH in the aeration basin was adjusted to between 7 and 8, the effluent NO_2^--N disappeared immediately.

Sludge Settling Characteristics. A problem encountered in some nitrification studies was that the MLSS maintained in the aeration basin was too low and effluent suspended solids were too high as a result of poor settling in the clarifier. Filamentous organisms grew at high loadings in the absence of trace nutrients[26,34]. In the present study, the activated sludge had good settling characteristics; the sludge volume index (the volume in mL occupied by 1g of a suspension after 30 minutes settling) (SVI) was around 100 mL/g (from 34 to 195) and no filamentous organisms were observed by microscopic examination. The MLSS in the aeration basin were maintained at 3000 mg/L (from 1560 to 4190). However, occasional sludge accumulations in the bottom of the clarifier because of problems with the sludge scraper and sludge recycle apparatus, resulted in denitrification and production of a large block of floating sludge which, in turn, temporarily led to high suspended solids in the effluent.

CONCLUSIONS

From the results of these investigations the following conclusions can be drawn:

- A single-stage activated sludge nitrification system can successfully remove ammonia-nitrogen from the effluent of an anaerobic filter treating 10% coal gasification wastewater containing as much as 600 mg TKN/L.

- Performance of the nitrification system was significantly dependent on the effluent quality of the anaerobic fluidized-bed activated carbon filter. Under the normal 32-day SRT and loadings of 0.15 kg NH_3-N MLVSS·day and 0.35 kg COD/kg MLVSS·day, removals of 97% TKN, 91% TOC and 95% COD were achieved.

- For effective nitrification of the coal gasification wastewater, solids retention time should be more than 22 days.

- Residual phenol and o-cresol could be completely removed in the nitrification system in all cases, but m-cresol and p-cresol removal depended on their influent concentrations. In some instances, the total amount of effluent m-cresol and p-cresol exceeded 15 mg/L and inhibition of the nitrification process occurred.

- Addition of powdered activated carbon to the nitrification system or periodic replacement of a portion of granular activated carbon in the anaerobic filter removed or reduced the concentration of the inhibitory compounds and eliminated inhibition of nitrification.

- Nitrogen balances indicated that the total effluent nitrogen accounted for 90.2% of influent TKN; the unaccounted nitrogen was attributed to microbial cell growth requirements and possible losses from denitrification, air stripping, and analytic error.

- Average alkalinity consumption was 5.8 mg alkalinity consumed/mg NH_3-N removed.

DENITRIFICATION STUDY

A 283-day study was conducted to study the denitrification of anaerobically treated and nitrified coal gasification effluent. The study was divided into three phases: 1 - acclimation; 2 - stable operation with a relatively constant mean cell residence time (MCRT) using methanol as an external carbon source; and 3 - stable operation with a relatively constant MCRT substituting phenol for methanol as the carbon source. During phase 2 of the operation, two-substrate limitations were imposed on the system. The first was nitrate limitation, where nitrate was not sufficiently available to bacteria for the oxidation of methanol. The second was methanol limitation, where methanol was not available in sufficient quantity for bacteria to reduce all of the nitrate-nitrogen in the influent. The summary of these phases are presented in Table 12.

Phase 1

During the first 99 days the system was acclimated to the use of nitrate from the nitrification reactor as a substrate. The concentration and total mass of suspended solids in the reactor during this period are presented in Figures 19 and 20. To accelerate this phase, i.e., acclimation, for a period of 19 days, some of the solids in the effluent were settled by gravity and returned manually to the reactor. The initial mass of suspended solids in the reactor was 5 g and concentration of suspended solids was 0.5 g/L, which remained relatively constant until Day 560, as presented in Figures 19 and 20. During this period, Day 541 to 560, the concentration of nitrate-nitrogen in the effluent decreased from 420 mg/L to 100 mg/L (see Figure 21), indicating that the microorganisms responsible for denitrification were acclimating and accumulating in the system. The TOC concentration in the influent ranged between 350 and 950 mg/L, and the TOC concentration in the effluent varied between 100 and 550 mg/L from Day 541 to 560 (see Figure 22). The large variation in TOC concentration in the influent is due to incomplete mixing of the methanol-water mixture, and is discussed in more detail later. The variation in the effluent TOC was a direct result of the varying influent TOC.

From Day 561 to 637, the concentration of solids increased from 0.5 g/L to 5.5 g/L (see Figure 19), and as a result, all the nitrate-nitrogen in the effluent disappeared, indicating that denitrifying microorganisms had accumulated to a sufficient level. The TOC concentration in the influent varied between 50 and 2300 mg/L and in the effluent ranged between 50 and 1250 mg/L during this period (these variations are due to the reason mentioned above). In addition, the contribution of TOC from the coal gasification wastewater is illustrated in Figure 22. As illustrated in Figure 22, the TOC concentration of coal gasification wastewater is much lower than the values of the total influent and effluent TOC concentration.

Phase 2

Phase 2 of the study began on Day 641 and continued for 134 days. During this phase, two-substrate limitations, nitrate-nitrogen and methanol, were imposed to study the performance of the denitrification under these conditions. From Day 641 to 775, a predetermined amount of solids were wasted from the reactor (see Figure 23). Due to this wastage, the concentration of suspended solids was maintained at a relatively constant level (see Figure 19). The total mass of solids lost during daily operation, as a result of solids lost in the effluent as well as those wasted directly from reactor, is presented in

Table 12. Summary of Denitrification Operational Phases

Phases	Type of Operation	Carbon Source	Period* (day)	Duration (day)
1	Acclimation	Methanol	541-640	99
2	Stable operation with a relatively constant MCRT	Methanol	641-774	134
3	Stable operation with a relatively constant MCRT	Methanol and Phenol	776-825	50

*Indicated period is consistent with day designation used on anaerobic filter portion of project, i.e., anaerobic filter operation was started on Day 1.

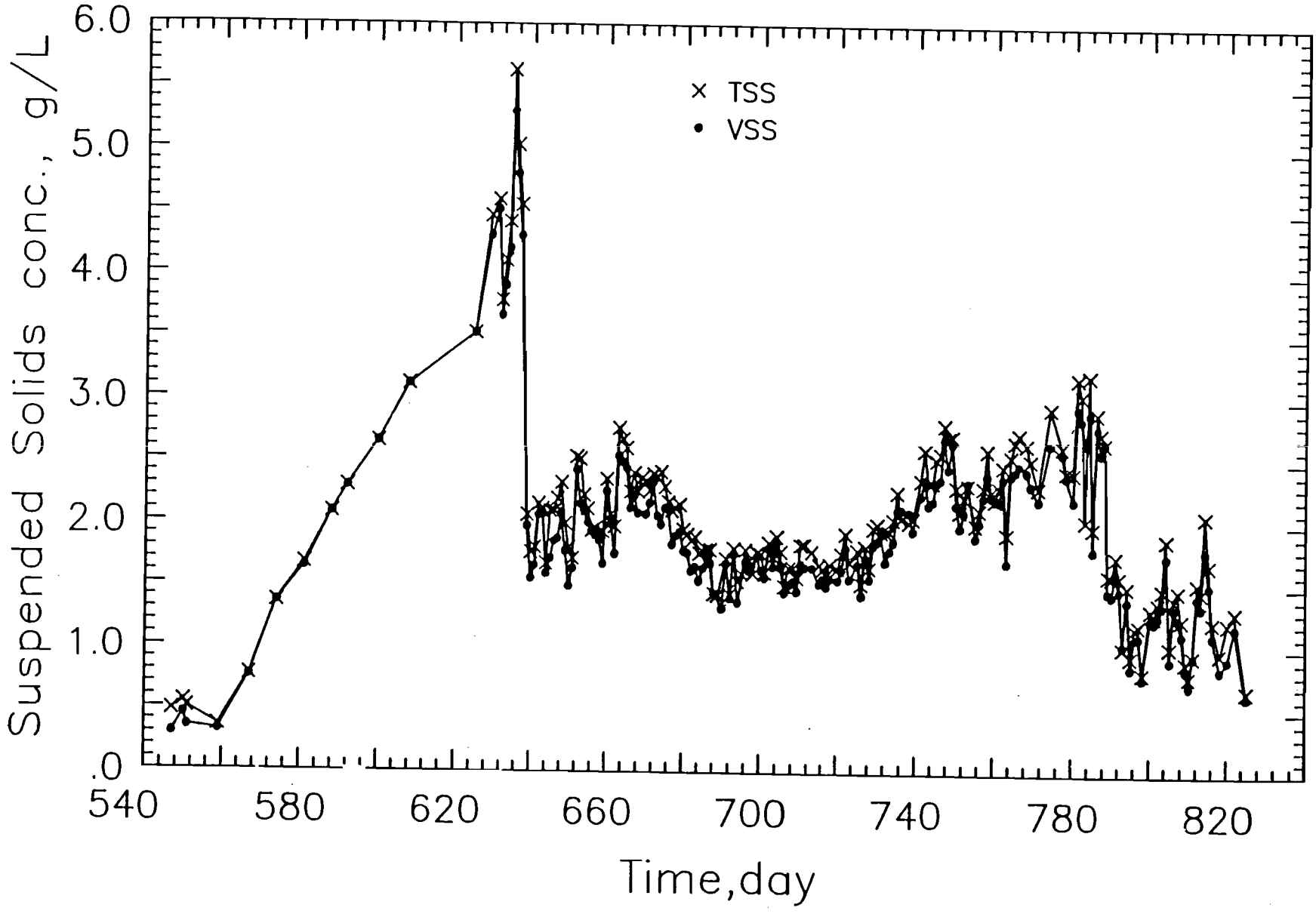

Fig. 19 Suspended Solids Concentration, Denitrification Reactor.

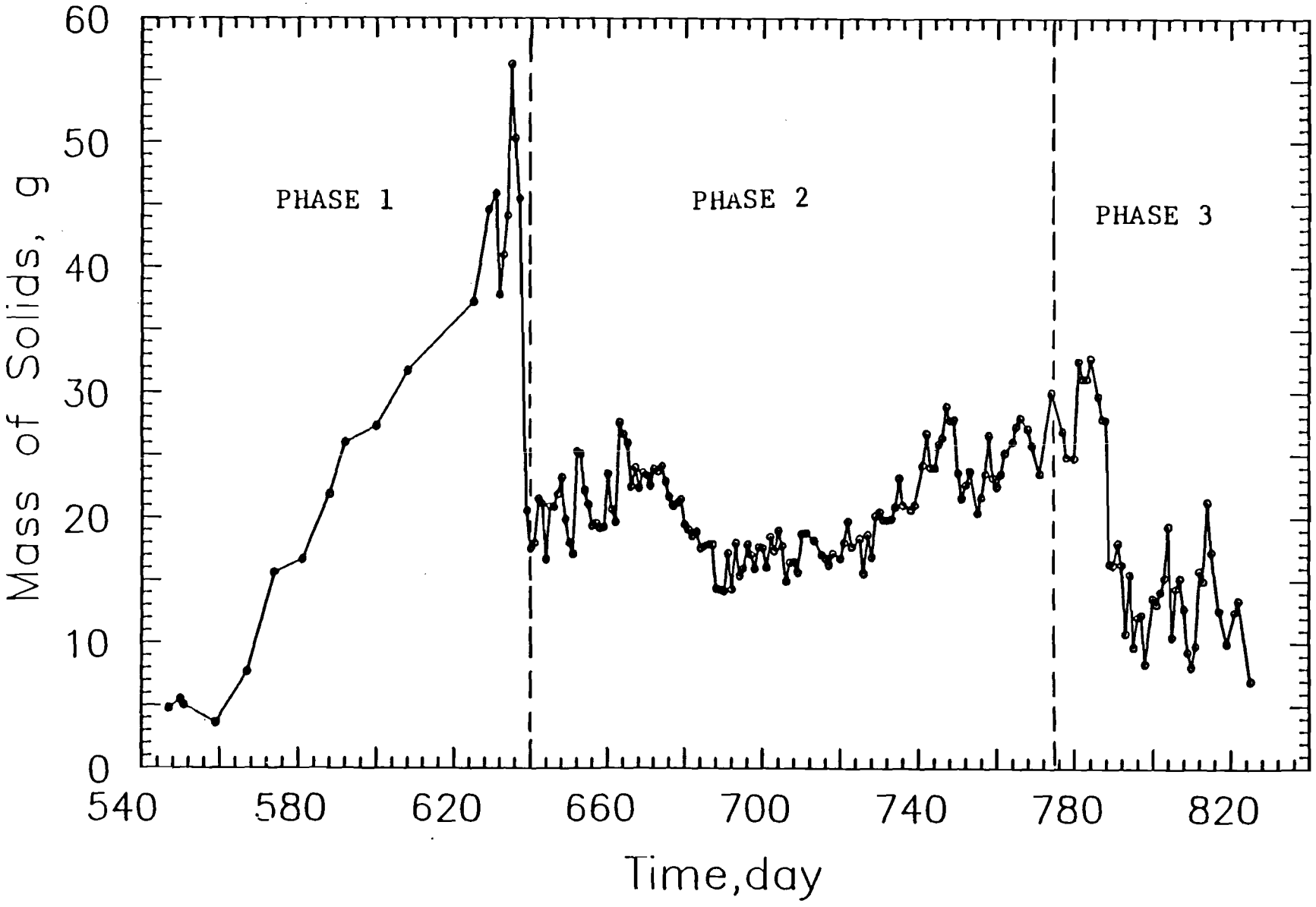

Fig. 20 Total Solids, Denitrification Reactor.

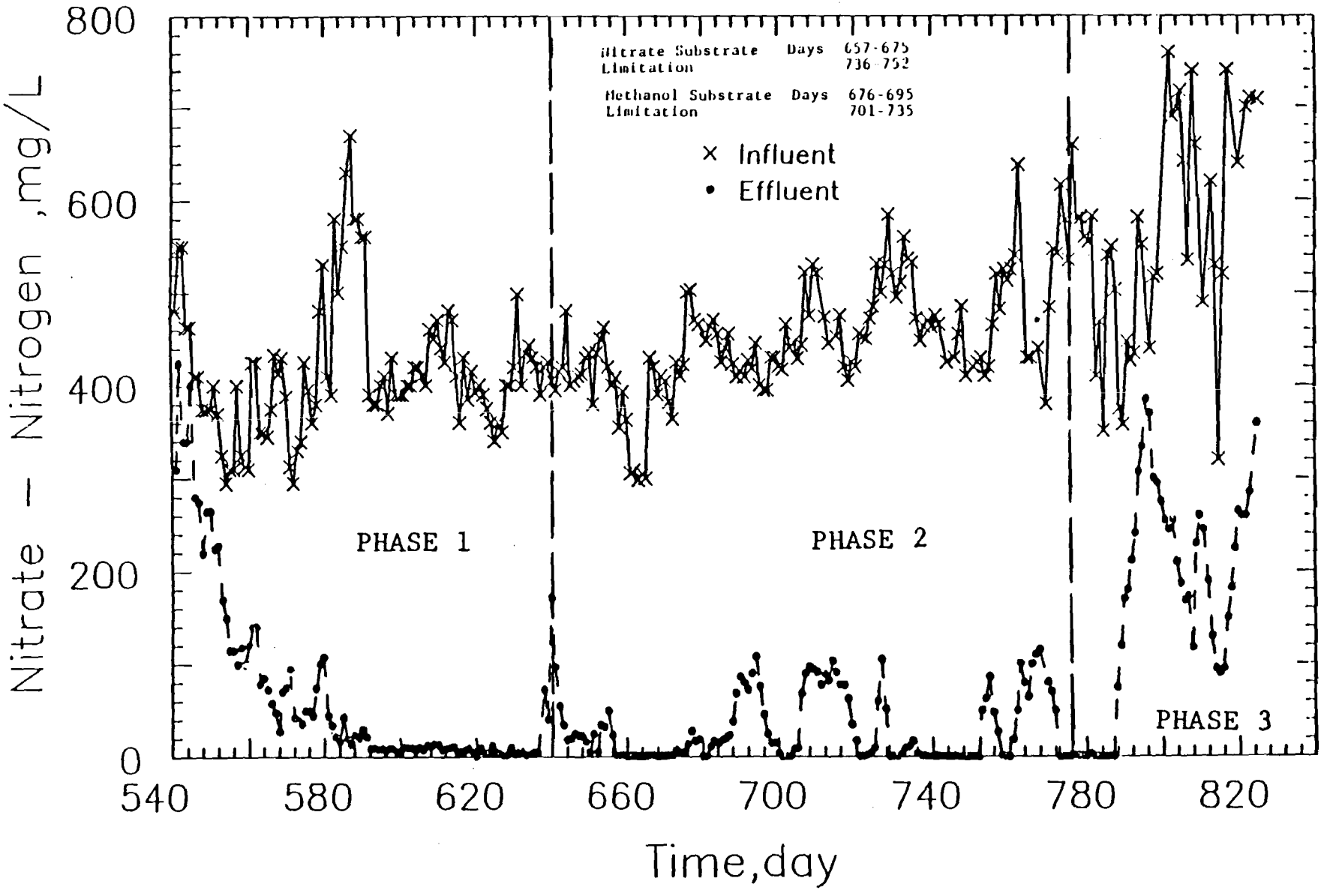

Fig. 21 Nitrate Concentration, Denitrification Reactor.

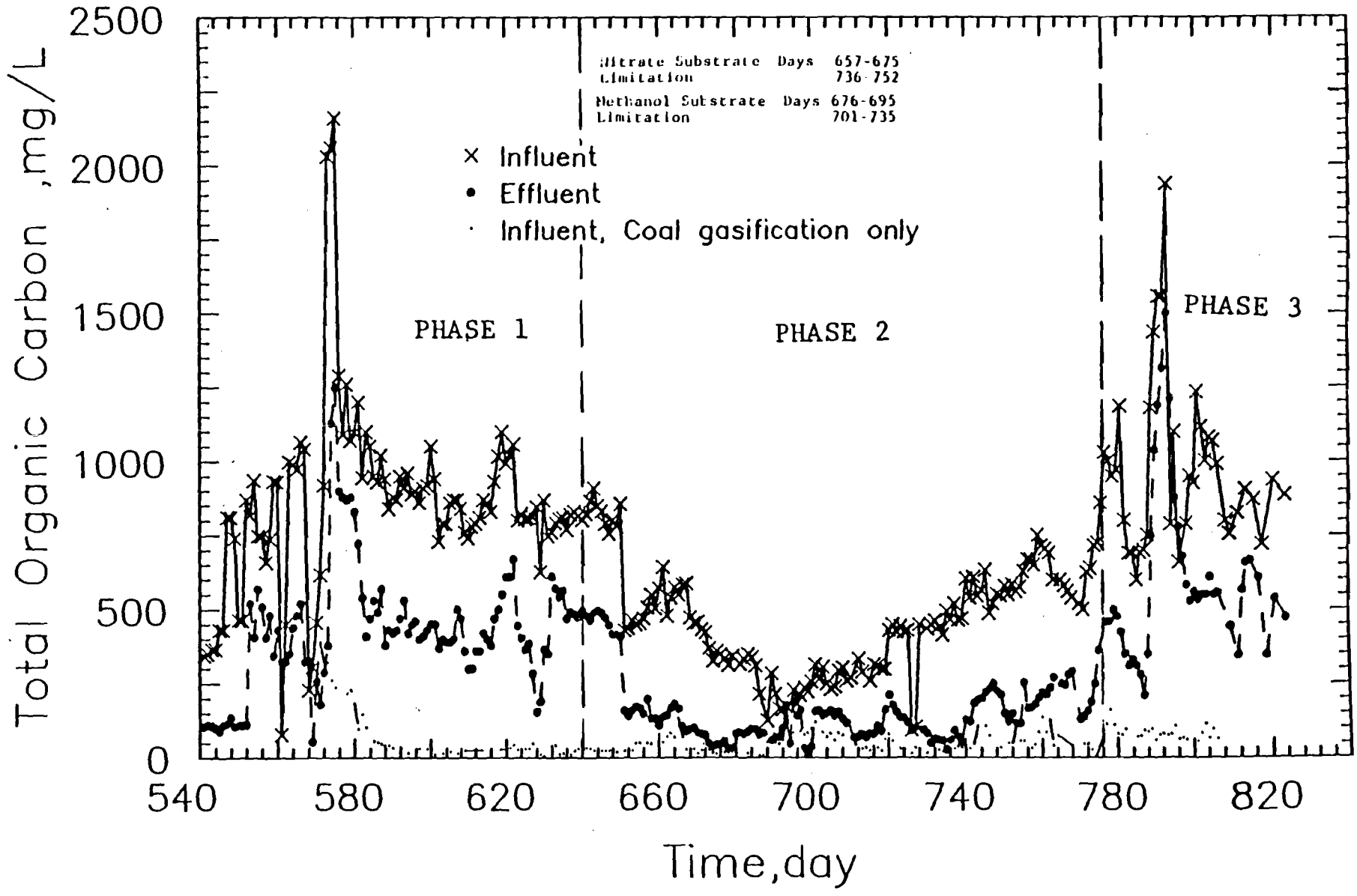

Fig. 22 Total Organic Carbon Concentration, Denitrification Reactor.

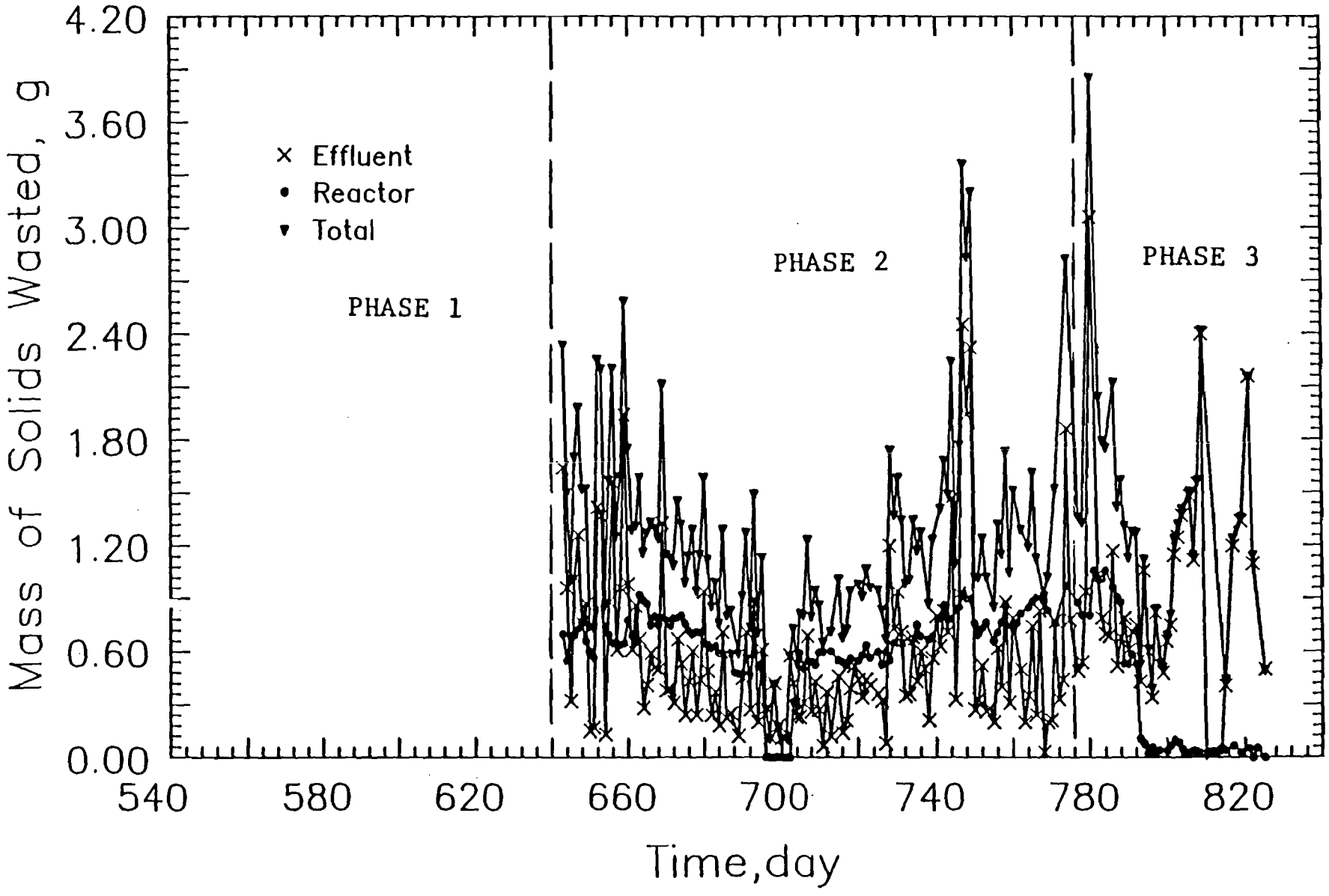

Fig. 23 Solid Wasted, Denitrification Reactor.

Figure 23. The concentration of total suspended solids lost in the effluent ranged between 5 and 380 mg/L (see Figure 24). The MCRT for this phase of operation is presented in Figure 25. During the period of Days 641-775, the MCRT ranged between 8 and 150 days, with an average of approximately 20 days.

During this phase of the operation, nitrate-nitrogen substrate limitation was imposed on the system, i.e., the nitrate flow rate (nitrification effluent) was maintained at a constant level but methanol was supplied at a decreased rate of 17.5 g/d. This rate corresponded to a ratio of 3.5 g methanol per g of nitrate-nitrogen, i.e., this ratio was deliberately chosen because it is in excess of theoretical ratio of 2.47 g methanol per g nitrate-nitrogen (McCarty et al.[36]). Due to the excess of methanol in the reactor, all the nitrate-nitrogen was removed from the effluent. The periods when nitrate-nitrogen was the limiting substrate, Days 657-675 and Days 736-752, are illustrated in Figures 21 and 22. During this substrate limitation, the concentrations of TOC in the influent and the effluent ranged between 450-750 mg/L and 50-250 mg/L, respectively (see Figure 22).

The second, and last, limitation imposed on the system during phase two of the operation, was a methanol limitation. The methanol feed rate was gradually reduced from 17.5 g/d to 10-12 g/d. This lower feed rate of methanol corresponded to a ratio of 2-2.4 g methanol/g nitrate-nitrogen. Since this ratio was below the theoretical ratio of 2.47 g methanol/g nitrate-nitrogen and there was less methanol available to the microorganisms to reduce the influent nitrate-nitrogen, the concentration of nitrate-nitrogen in the effluent increased. The periods for which methanol was the limiting substrate, i.e., Days 676-695 and 701-735, are illustrated in Figures 21 and 22. During this substrate limitation, nitrate-nitrogen concentration in the effluent increased from 0 to 250 mg/L, the TOC concentration in the influent was gradually reduced from 500 to 150 mg/L and the resulting effluent concentration dropped from 220 to 40 mg/L (see Figures 21 and 22).

Daily pH measurements of the system during phase 2 are presented in Figure 26. The pH of the influent and the reactor during this phase of operation varied between 6.5 to 8.4 and 8.95 to 9.37, respectively. The pH of the effluent was almost the same as the pH of the reactor (i.e., 1-2% variation).

The alkalinity of the influent and the effluent is illustrated in Figure 27. During this phase of operation, the average values for the influent and the effluent alkalinity were 530 and 1510 mg/L as $CaCO_3$, respectively. The temperature of the reactor was maintained at ambient temperature and varied in extreme from 16 to 30°C with the average temperature of 22 to 25°C (see Figure 28).

Phenol Substitution

During the last phase of the study, beginning on Day 776, methanol was replaced by phenol as the external carbon source and MCRT was maintained at approximately 20-day (see Figure 25). The amount of organic carbon required to reduce the nitrate-nitrogen was determined by performing a mass balance on the system and on a gradual basis, phenol was substituted for methanol. For example, during the initial period, if 4 g of organic carbon was needed to reduce 1 g of nitrate-nitrogen, 60% or 2.4 g of organic carbon was supplied as methanol and the rest, 40% or 1.6 g of organic carbon, was used as phenol.

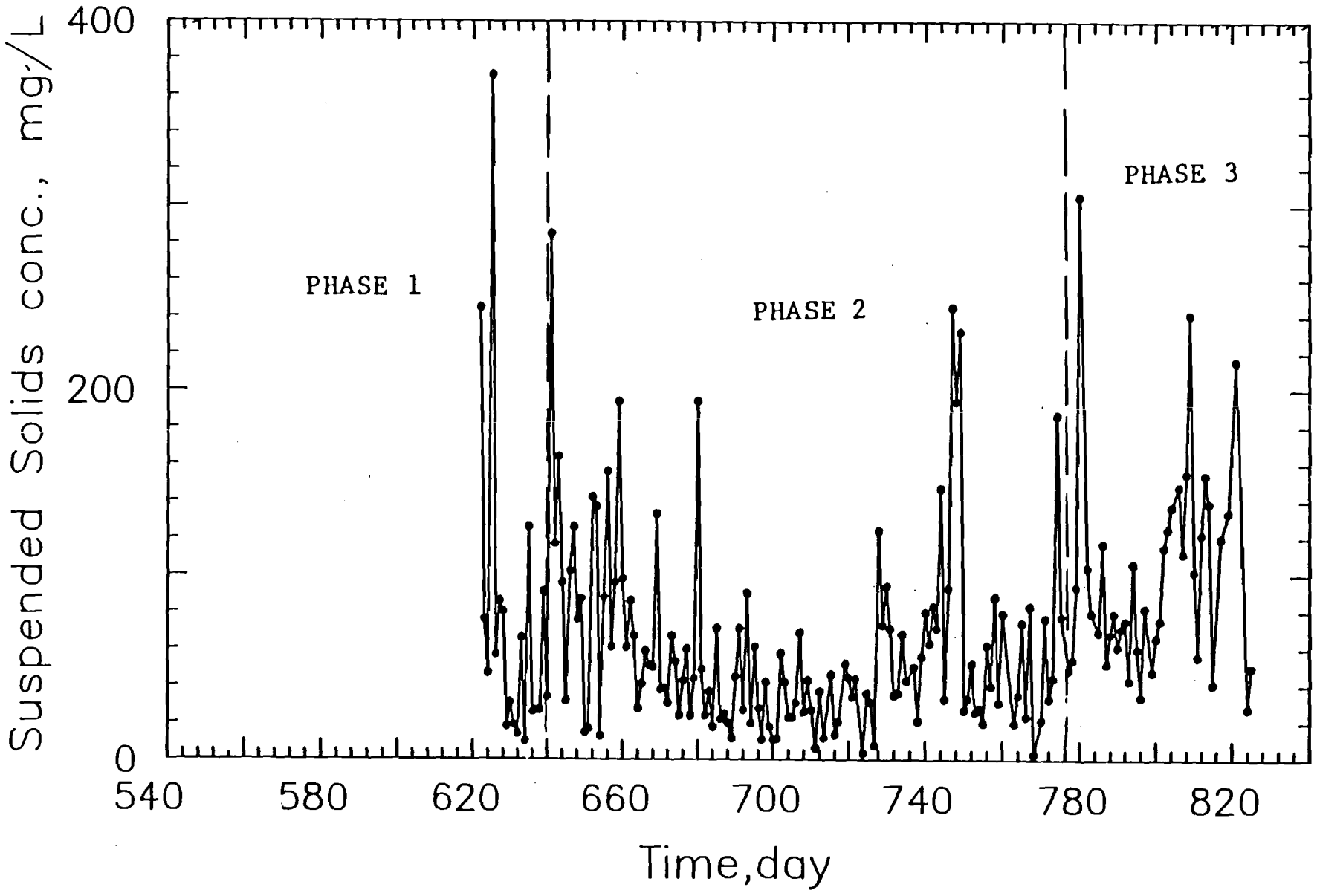

Fig. 24 Effluent Suspended Solids, Denitrification Reactor.

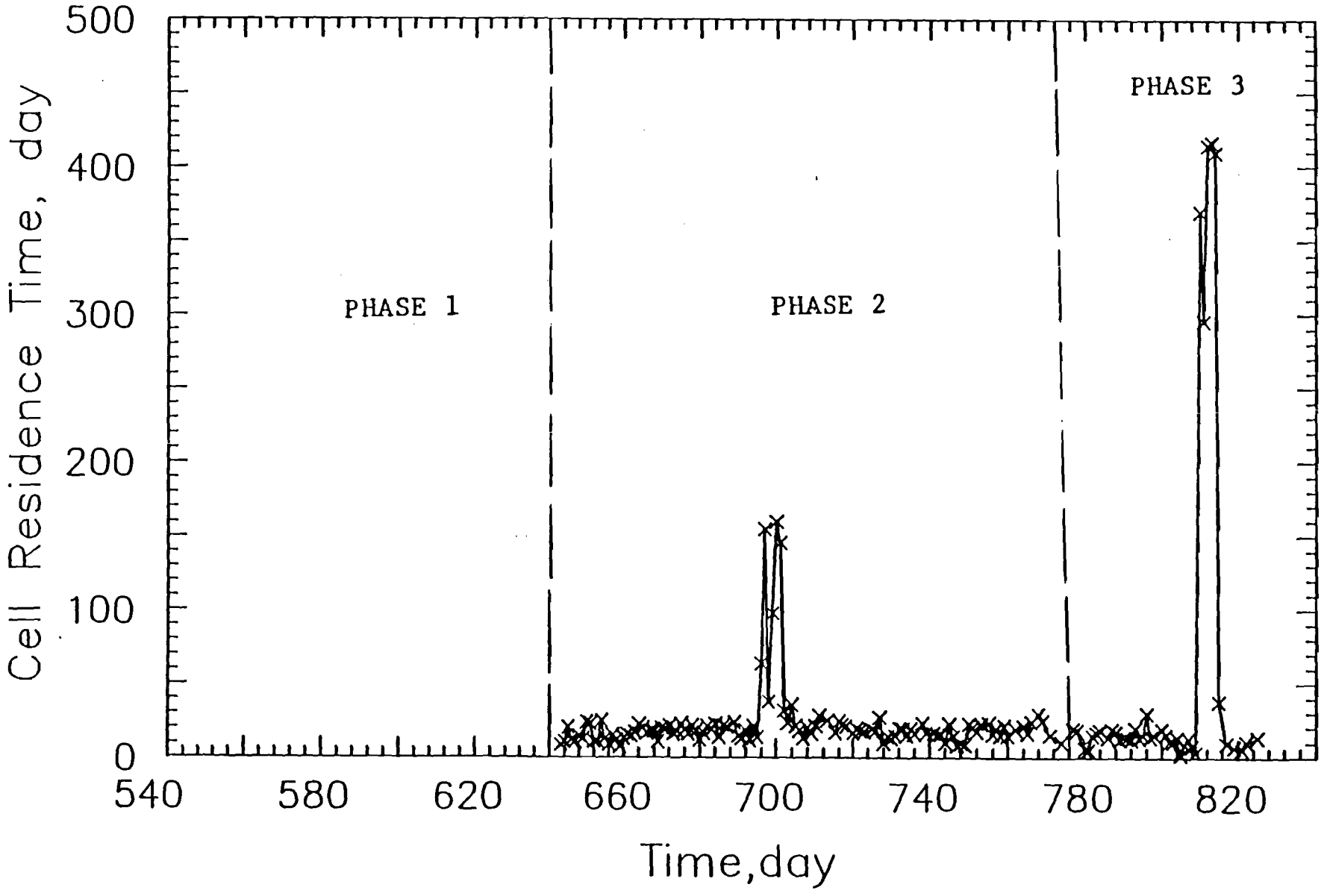

Fig. 25 Cell Residence Time, Denitrification Reactor.

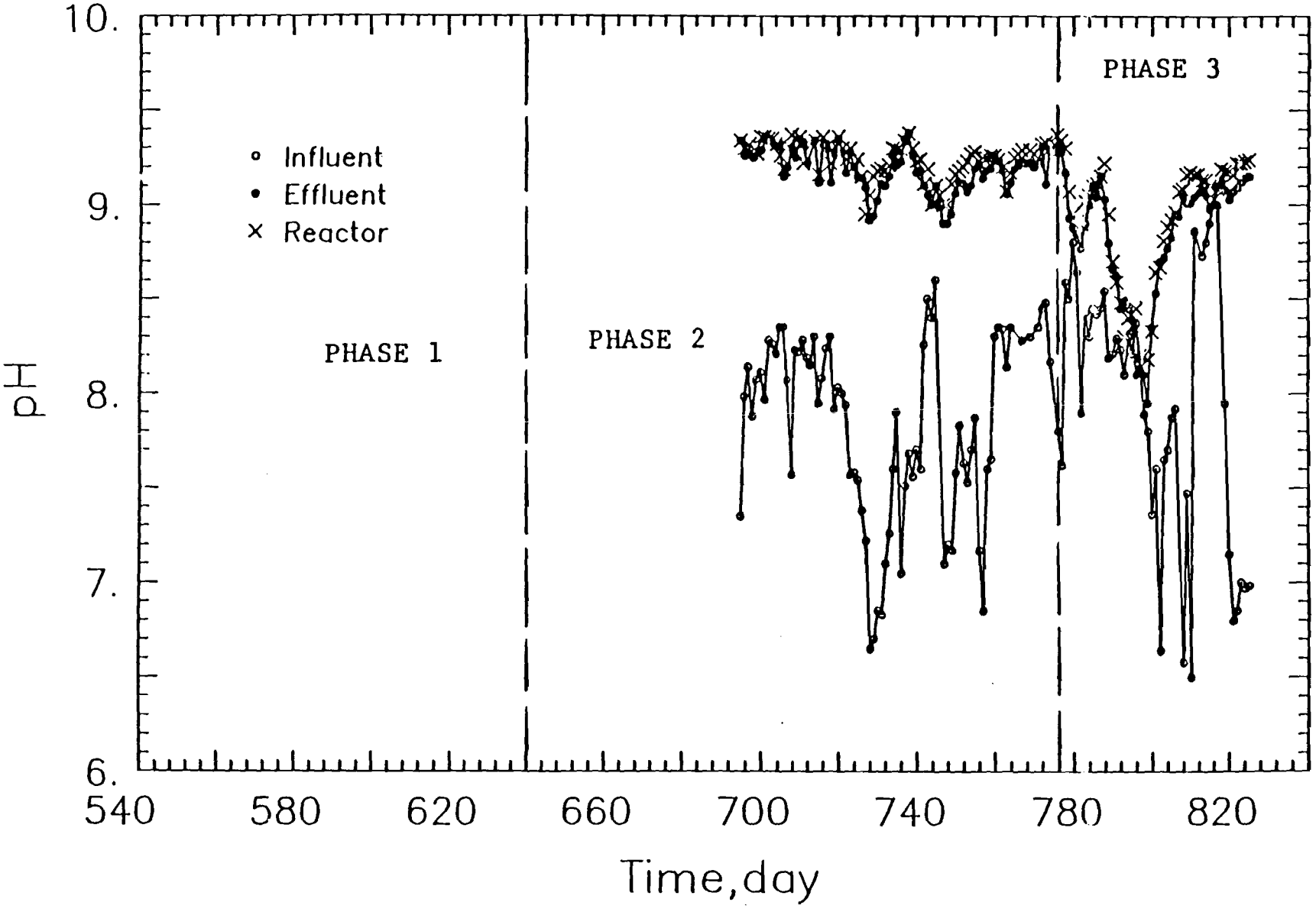

Fig. 26 pH, Denitrification Reactor.

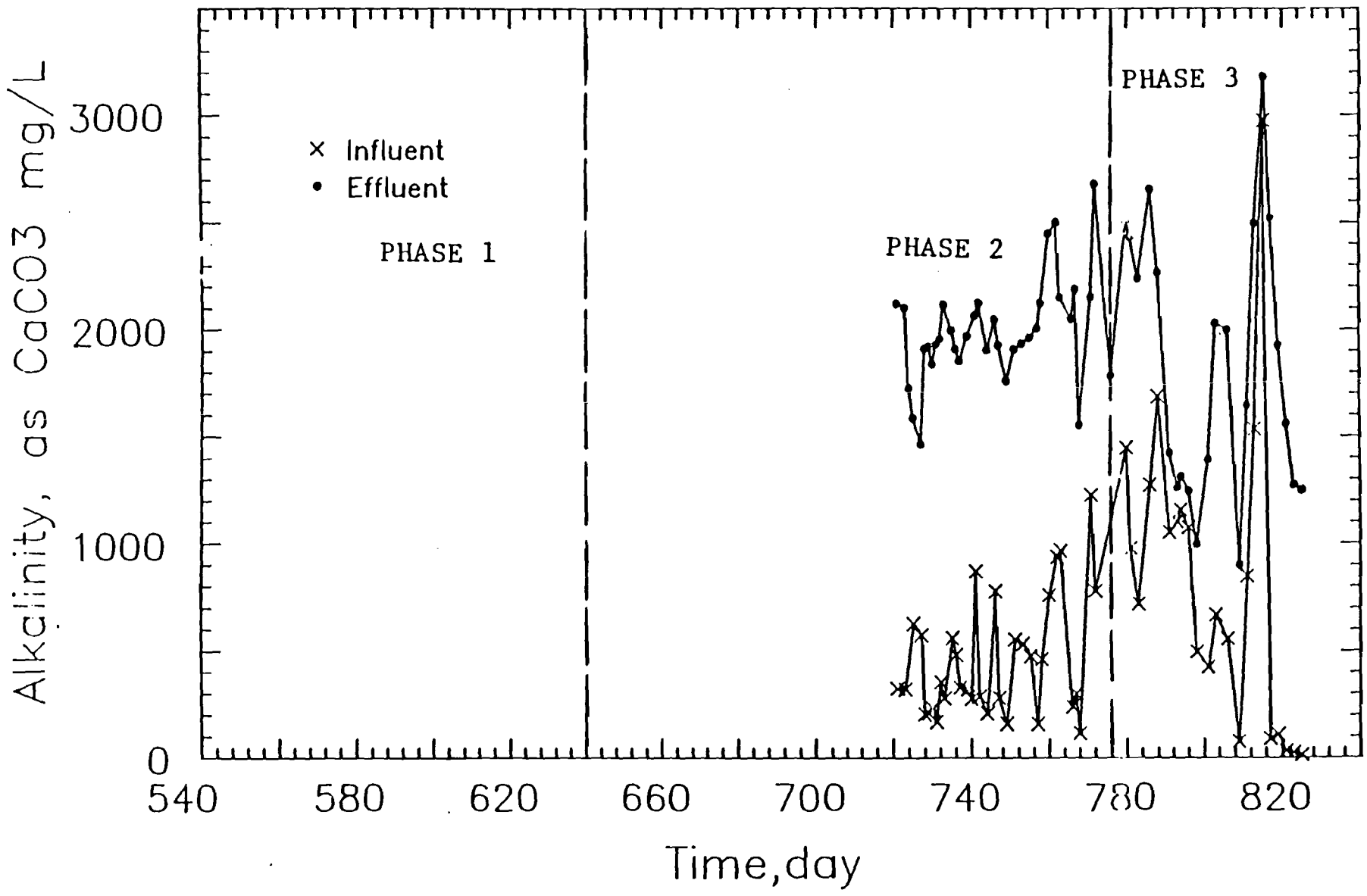

Fig. 27 Alkalinity, Denitrification Reactor.

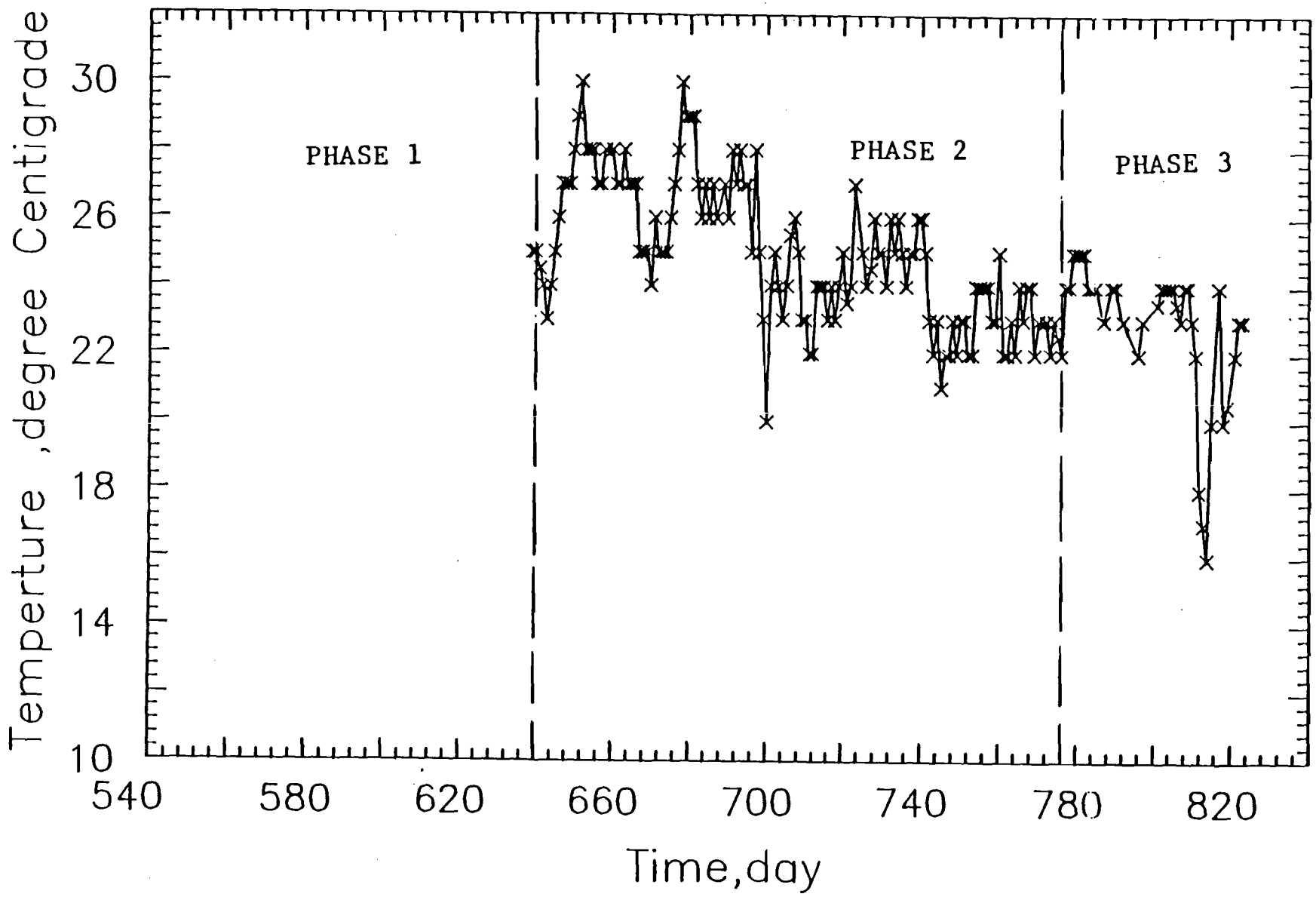

Fig. 28 Temperature, Denitrification Reactor.

The phenol substitution steps for this phase of the operation were as follows: 1) 100% methanol-30% phenol; 2) 60% methanol-40% phenol; 3) 20% methanol-80% phenol; 4) 0% methanol-100% phenol; 5) 269% phenol; 6) 122% phenol; 7) 100% phenol; 8) 90% phenol-10% methanol; 9) 70% phenol-30% methanol; and, 10) 50% phenol-50% methanol. These substitutions of phenol for methanol are illustrated in Figure 29.

100% Methanol - 30% Phenol. In the first substitution step, the mass of organic carbon to reduce all the nitrate in influent was determined and 100% of that was supplied as methanol. Phenol was supplied as a 30% excess of organic carbon. This period lasted 6 days, beginning on Day 776. All influent nitrate-nitrogen was removed and the total mass of solids in the reactor remained relatively stable at 25-35 g (see Figure 20). The pH of the reactor varied between 8.95 and 9.37. The influent and effluent TOC concentrations were 1000 and 1400 mg/L, respectively.

60% Methanol - 40% Phenol. During the next 5 days, phenol was used as the organic carbon, and was supplied as 40% of the TOC required to reduce a unit mass of nitrate-nitrogen. The effluent concentration of nitrate-nitrogen remained unchanged, i.e., the concentration was almost zero. The pH of the reactor ranged between 8.95 and 9.37 and the influent and effluent TOC concentrations were 600-800 mg/L and 300-400 mg/L, respectively (Figures 26 and 22). The concentration of solids in the reactor was approximately 2.5-3.5 g/L.

20% Methanol - 80% Phenol. The mass of phenol was increased from 40% of the TOC to 80% of the TOC during Days 787-788. The performance of the system remained relatively unchanged, i.e., the pH, mass of solids, MCRT, and nitrate-nitrogen in the effluent remained stable.

100% Phenol. For the next three days, 789-791, phenol was used as the sole source of carbon. Due to this increase in phenol mass, the pH decreased to 8.6 and the concentration of solids in the reactor decreased from 2.3 to 1.6 g/L. The concentration of nitrate-nitrogen in the effluent started increasing on Day 789 (Figure 21).

269% Phenol. For one day the mass of organic carbon added to reactor was increased by 269%, i.e., the organic carbon mass was increased from 6.8 to 18.3 g or the phenol mass was increased from 8.9 to 23.9 g.

The resulting pH of the reactor decreased to 8.2 and nitrate-nitrogen concentration increased to 200 mg/L in the effluent.

122% Phenol. For the next period, Days 793-794, the mass of organic carbon was reduced to 122%, i.e., the organic carbon mass was decreased from 18.3 to 8.3 g or phenol mass was decreased from 23.9 to 10.87 g. The resulting pH of the reactor was 8.7 and 8.6 during these two days.

100% Phenol. During the next three days, 795-797, the mass of organic carbon was reduced by 22.0%, i.e., the mass of organic carbon was decreased from 8.3 to 6.8 g or phenol mass was reduced from 10.87 to 8.9 g. The concentration of nitrate-nitrogen in the effluent increased to 380 mg/L and the pH of the reactor was about 8.4.

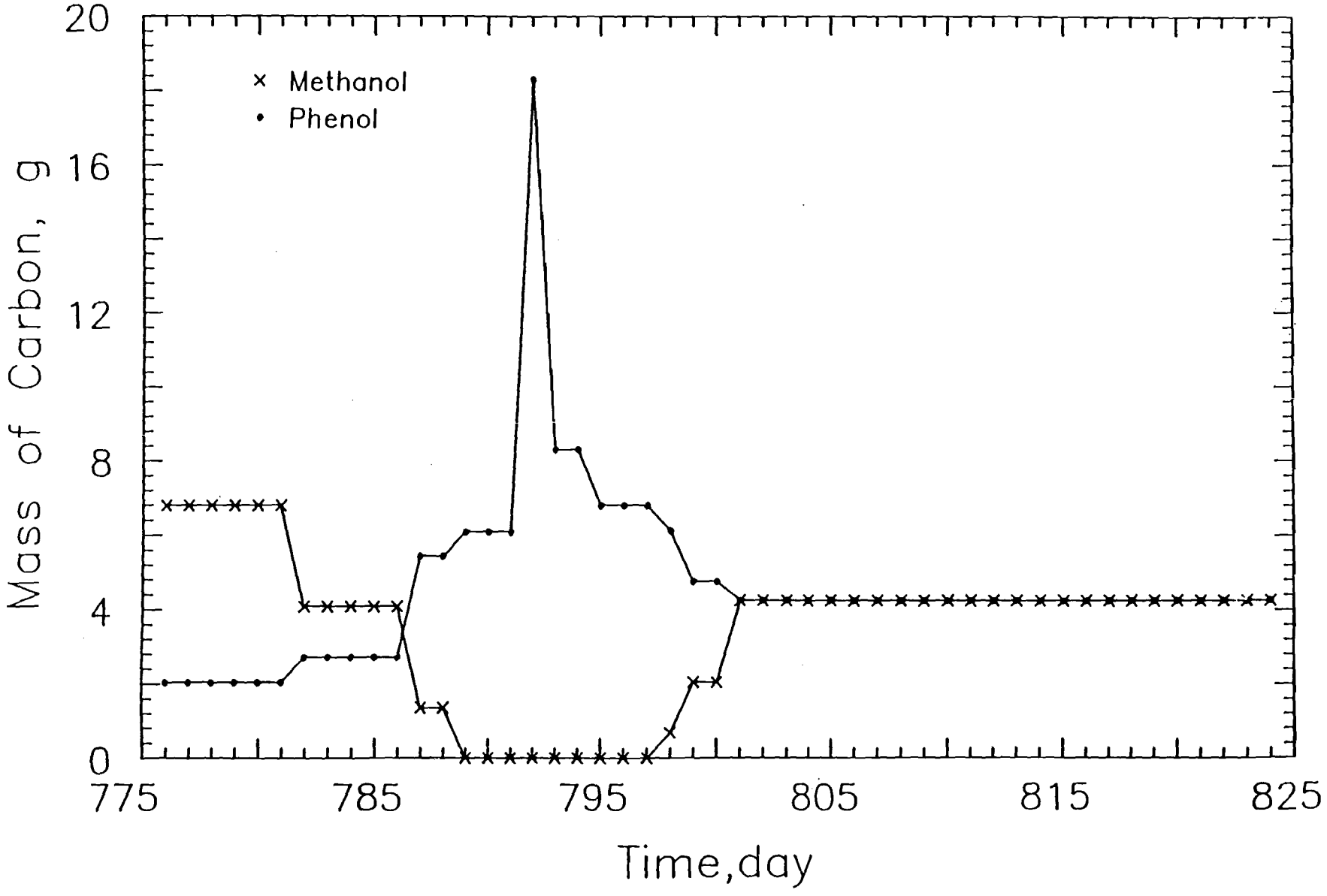

Fig. 29 Carbon Feed Composition - Phase 3 - Denitrification Reactor.

10% Methanol - 90% Phenol. For Day 798, 10% of the TOC was supplied as methanol and the rest as phenol, i.e., 0.68 and 6.12 g of carbon as methanol and phenol, respectively. The nitrate-nitrogen concentration in the effluent remained above 300 mg/L.

30% Methanol - 70% Phenol. During the Days 799-800, 30% of the TOC was supplied as methanol and the rest as phenol, i.e., 2.04 and 4.76 g of carbon as methanol and phenol, respectively. The nitrate-nitrogen concentration in the effluent decreased to 290 mg/L.

50% Methanol - 50% Phenol. During the next twenty-five days, beginning on Day 801, 50% of the TOC was supplied as methanol and the rest as phenol, i.e., 4.25 g of carbon as phenol and methanol. At the beginning of this period the concentration of influent to the anaerobic filter was increased, and as a result the nitrate-nitrogen concentration of the influent increased from 500-550 to 700-750 mg/L and consequently the organic carbon concentration increased to 800-900 mg/L.

The pH of the reactor steadily returned to a range of 9-9.2 and the nitrate-nitrogen concentration in the effluent was reduced to 100 mg/L due to decrease in the influent nitrate-nitrogen concentration. However, as the influent nitrate-nitrogen concentration increased to 700 mg/L the effluent concentration increased to 300-400 mg/L. Daily pH measurements of the system during Phase 3 is presented in Figure 26. The pH of the influent and reactor varied between 6.5 - 9.0 and 8.2 - 9.25, respectively. Daily alkalinity measurements of the system during Phase 3 are presented in Figure 27. The alkalinity of the influent and effluent varied between 300-2900 and 900-3200 mg/L as $CaCO_3$, respectively. The temperature of the reactor ranged from 16 to 26°C and is presented in Figure 28.

CONCLUSIONS

Based on the results from the suspended growth denitrification of the anaerobically treated-nitrified coal gasification wastewater, the following conclusions are made.

1. Suspended growth denitrification using methanol with cell recycle can be used to remove virtually 100% of the nitrate-nitrogen from anaerobically treated and nitrified coal-gasification wastewater.

2. The anaerobically treated and nitrified coal gasification wastewater had an insignificant amount of TOC, therefore, it was necessary to use an external carbon source, e.g., methanol, to reduce nitrate in the nitrified coal gasification wastewater.

3. One-hundred percent removal of nitrate-nitrogen was achieved at a ratio of 2.45 g of methanol per g of nitrate-nitrogen, a 20-day cell residence time, a 24-hour hydraulic retention time; the pH of the reactor ranged between 8.95-9.35 during this operation.

4. The pH of the nitrification effluent in the range of 6.0-8.5 had an insignificant effect on the denitrification performance, i.e., the nitrate removal did not change.

5. The pH of the reactor and alkalinity production were directly related to the nitrate-nitrogen and methanol concentration in the influent, i.e., high concentration in the influent resulted in more production of hydroxide ion and alkalinity.

6. Increasing the methanol flow rate resulted in instantaneous reduction in the nitrate concentration in the influent or vice versa.

7. Phenol can be partially substituted for methanol as the external carbon source. However, the inhibitory effect of phenol was observed when 100% phenol was used at a concentration of 600-700 mg/L. As a result the nitrate removal was reduced to 20-30% and the pH decreased to 8.2-8.3.

INHIBITION STUDY

Serum Bottle inhibition studies were carried out utilizing the mixed liquor from an active anaerobic activated carbon reactor and ten compounds found in coal gasification effluent at relatively high concentrations. Table 13 summarizes the results of the study, while Figures 30 and 31 show the results of the addition of phenol and raw wastewater to the mixed liquor.

As can be seen in Figures 30 and 31 the addition of phenol or raw wastewater does not appear to cause any inhibition of gas production.

Figures 32, 33, and 34 show that the addition of hydantoins to the mixed liquor do not inhibit gas production and the sample containing the additional substrate produce more gas than these without the additional substrate.

The addition of the cresol isomers had no effect on the gas production, indicating no inhibition. However, the addition of any of the picolines caused complete cessation of gas production indicating either severe inhibition and/or toxicity. Individual concentration of picolines and pyridines found in the raw wastewater is approximately 5-10 mg/L with a total concentration of approximately 20 to 25 mg/L. Therefore, accumulation of these materials by the granular activated carbon could result in severe inhibition of the microbiological system.

Continuous Flow Anaerobic Activated Carbon Filter Treatment of Pretreated Wastewater

In conjunction with the serum bottle inhibition studies an activated carbon filter was operated with dilute pretreated wastewater as the feed. The system was operated for a period of 200 days with limited success. Figure 35 shows the performance of the filter in terms of TOC removal. Although the feed substrate was primarily hydantoins from the pretreated wastewater, only 40 to 60% of the TOC was removed and gas production during the entire period averaged less than 1 L/d. Although extensive efforts were expended in searching for gas leaks, none were found. The lack of gas production coupled with the 40 to 60% TOC removal indicates the predominant removal mechanism was adsorption of the TOC onto the granular activated carbon. Total hydantoin removal for the period averaged 60%.

Table 13. Gas Production Inhibition by Coal Gasifier Effluent Constituents

Compound	Concentration mg/L	Results
phenol	280	No inhibition
o-cresol	150	No inhibition
m-cresol	150	No inhibition
p-cresol	150	No inhibition
hydantoin	200	No inhibition
5,5-dimethylhydantoin	800	No inhibition
5-methyl-5-ethylhydantoin	260	No inhibition
2-picoline	25 to 75	Complete inhibition
3-picoline	25 to 75	Complete inhibition
4-picoline	25 to 75	Complete inhibition

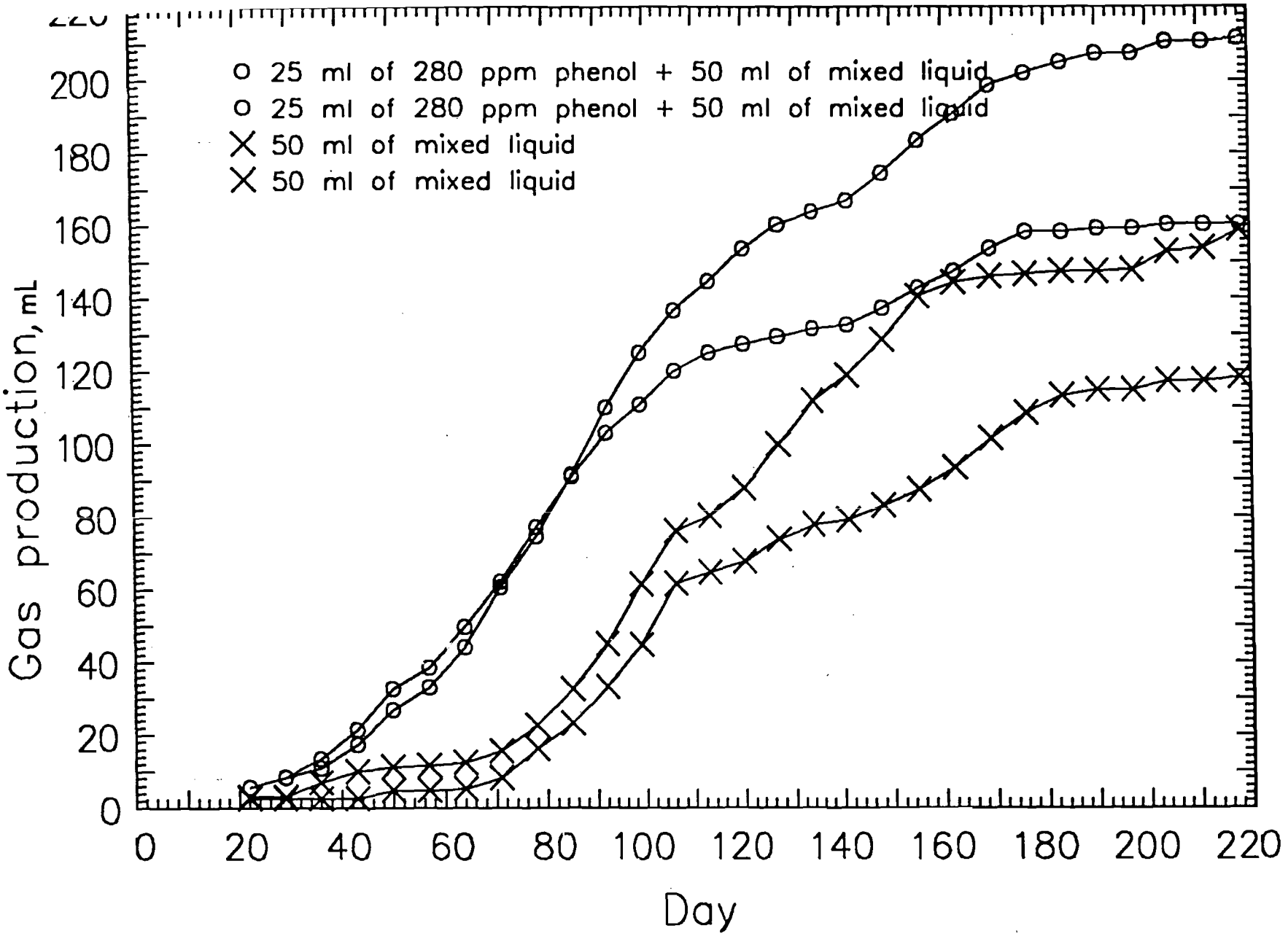

Fig. 30 Effect of Phenol Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

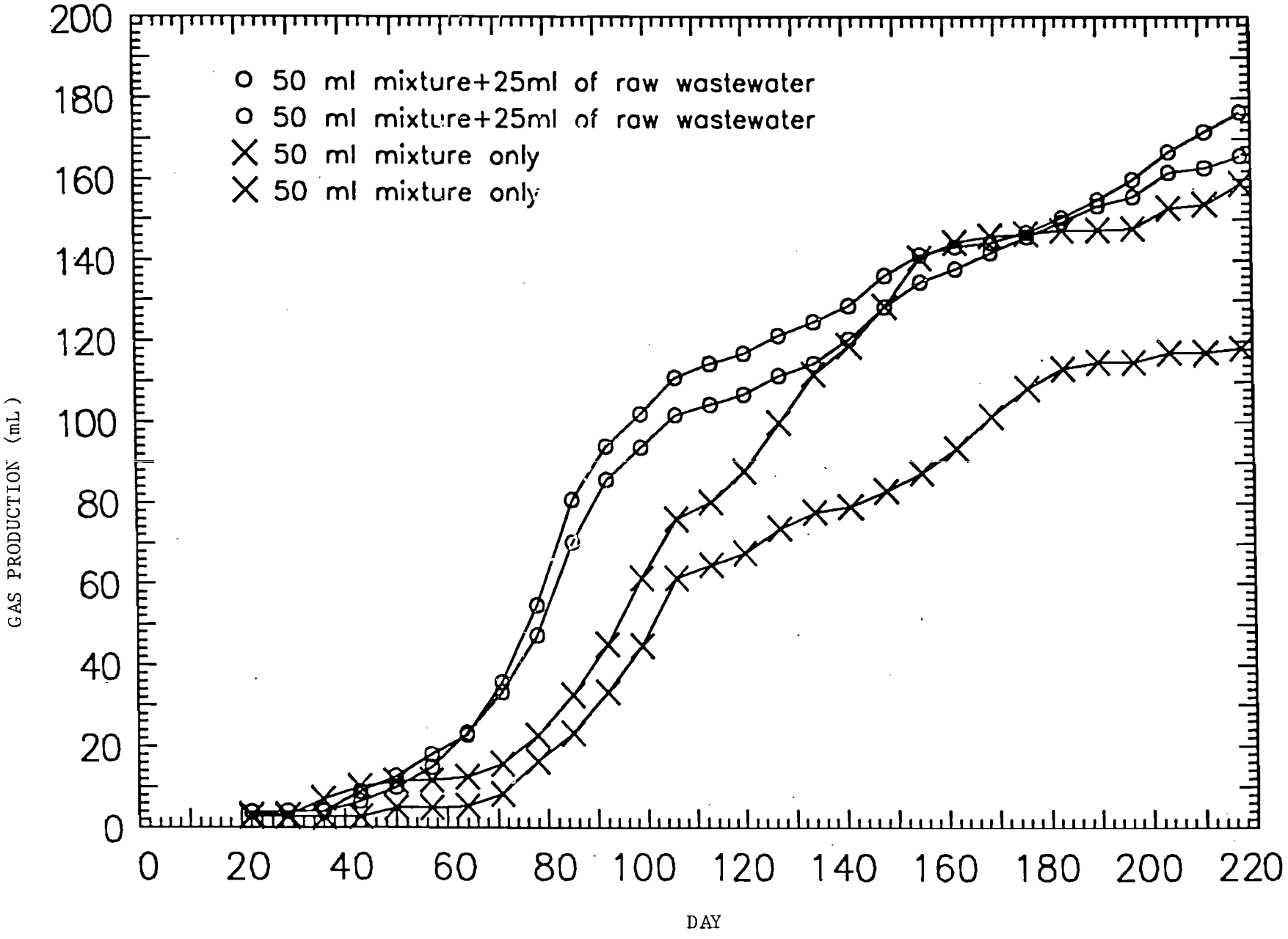

Fig. 31 Effect of Raw Wastewater Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

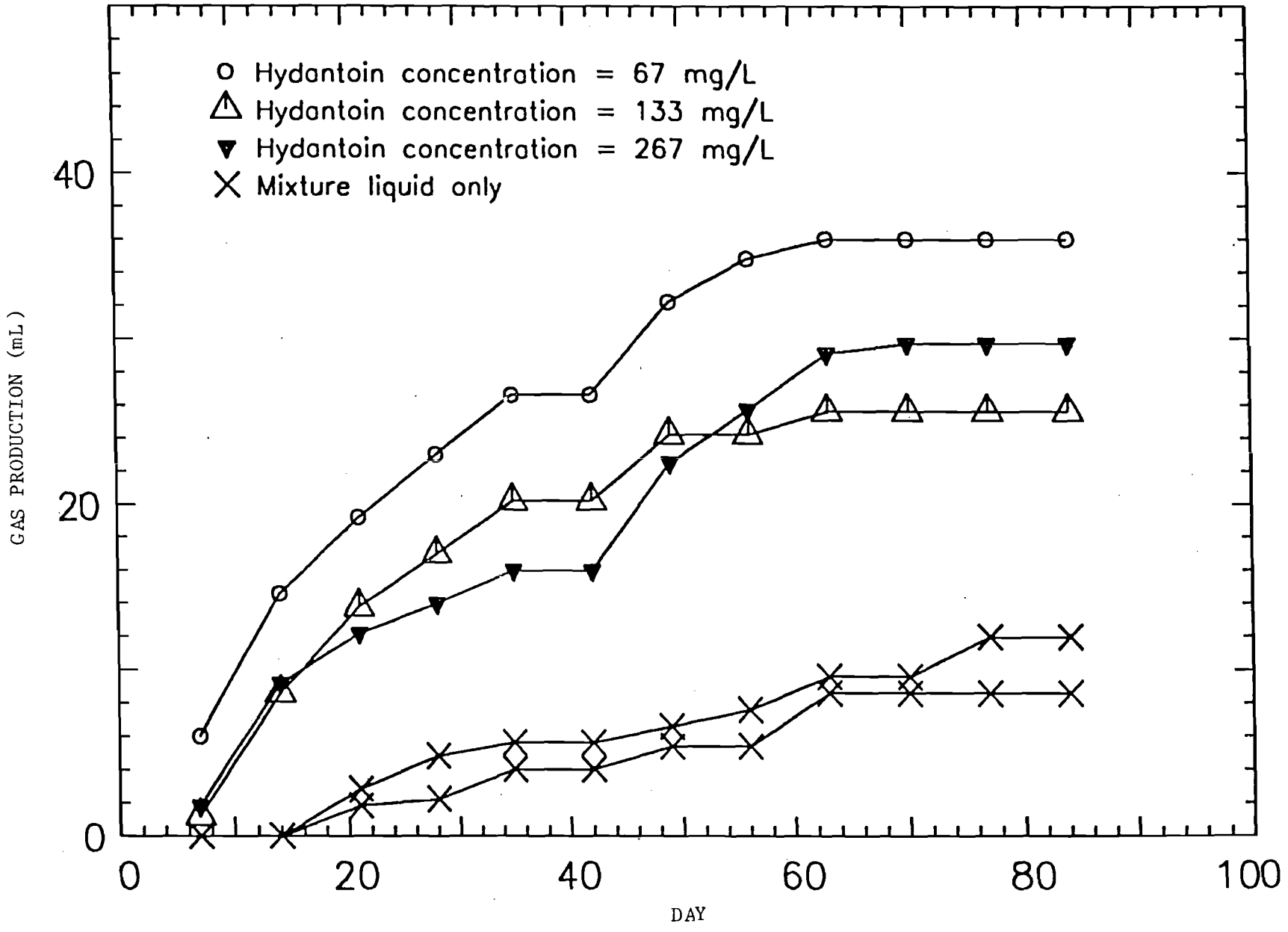

Fig. 32 Effect of Hydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

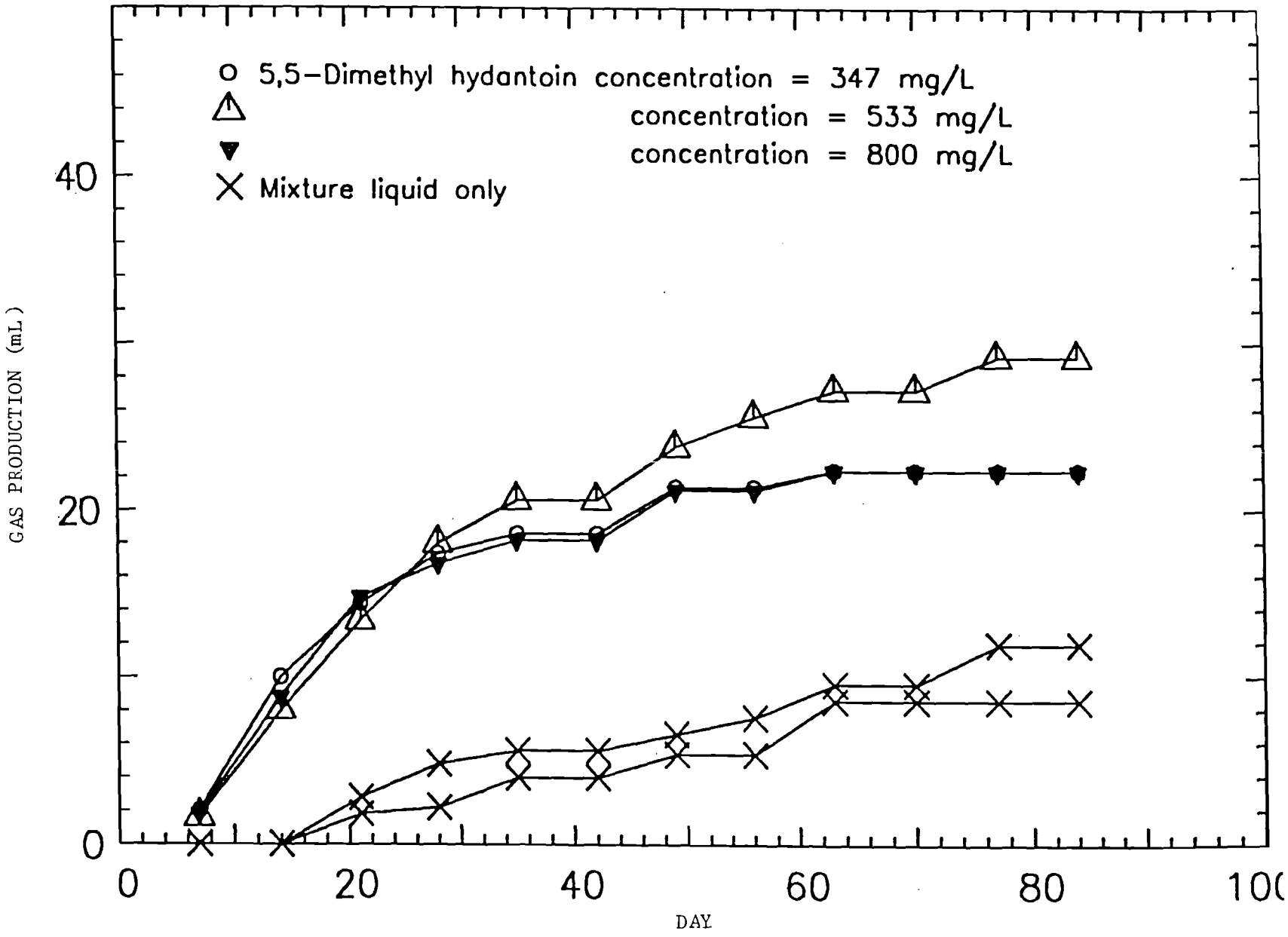

Fig. 33 Effect of 5,5-Dimethylhydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

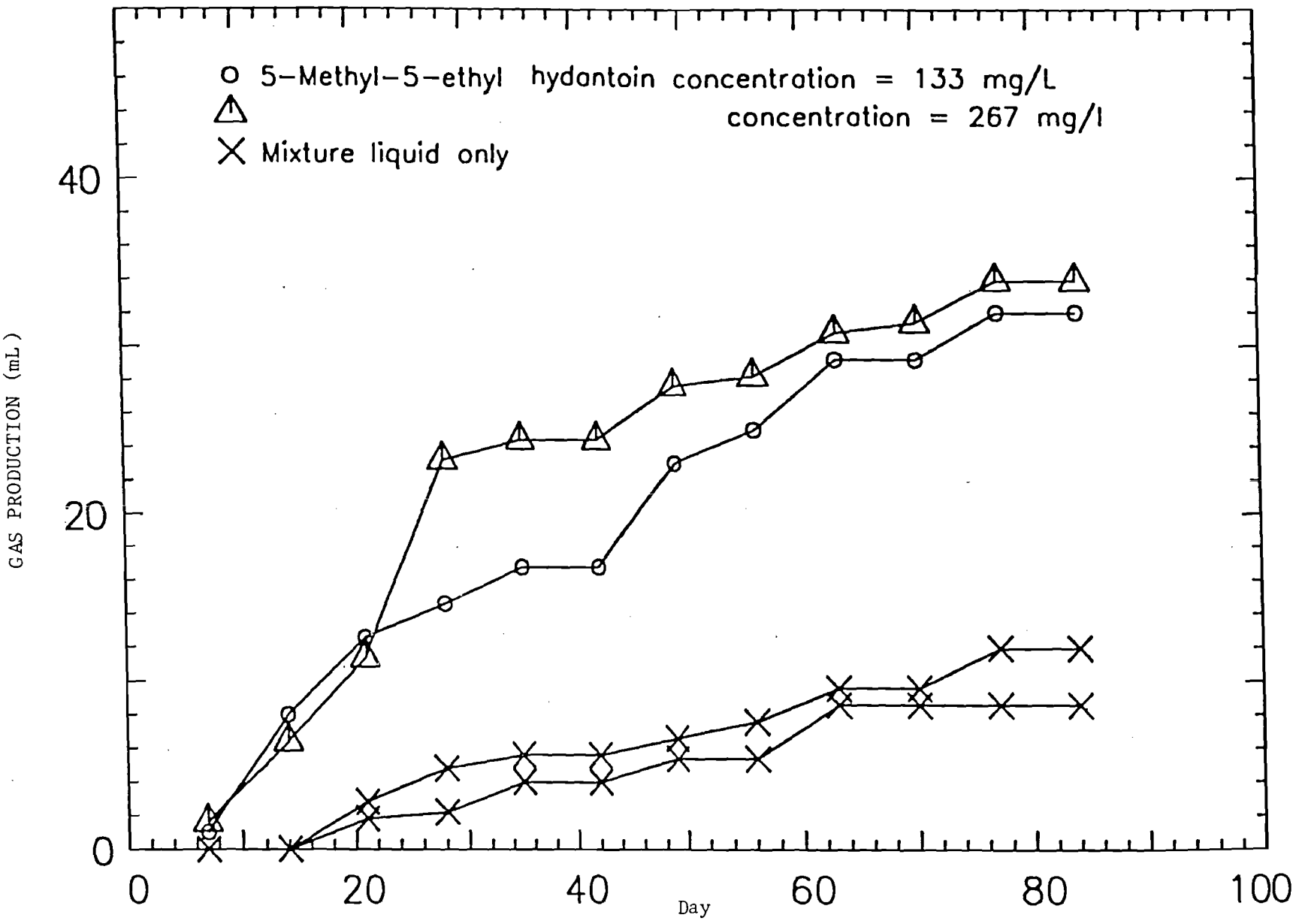

Fig. 34 Effect of 5-Methyl-5-Ethylhydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

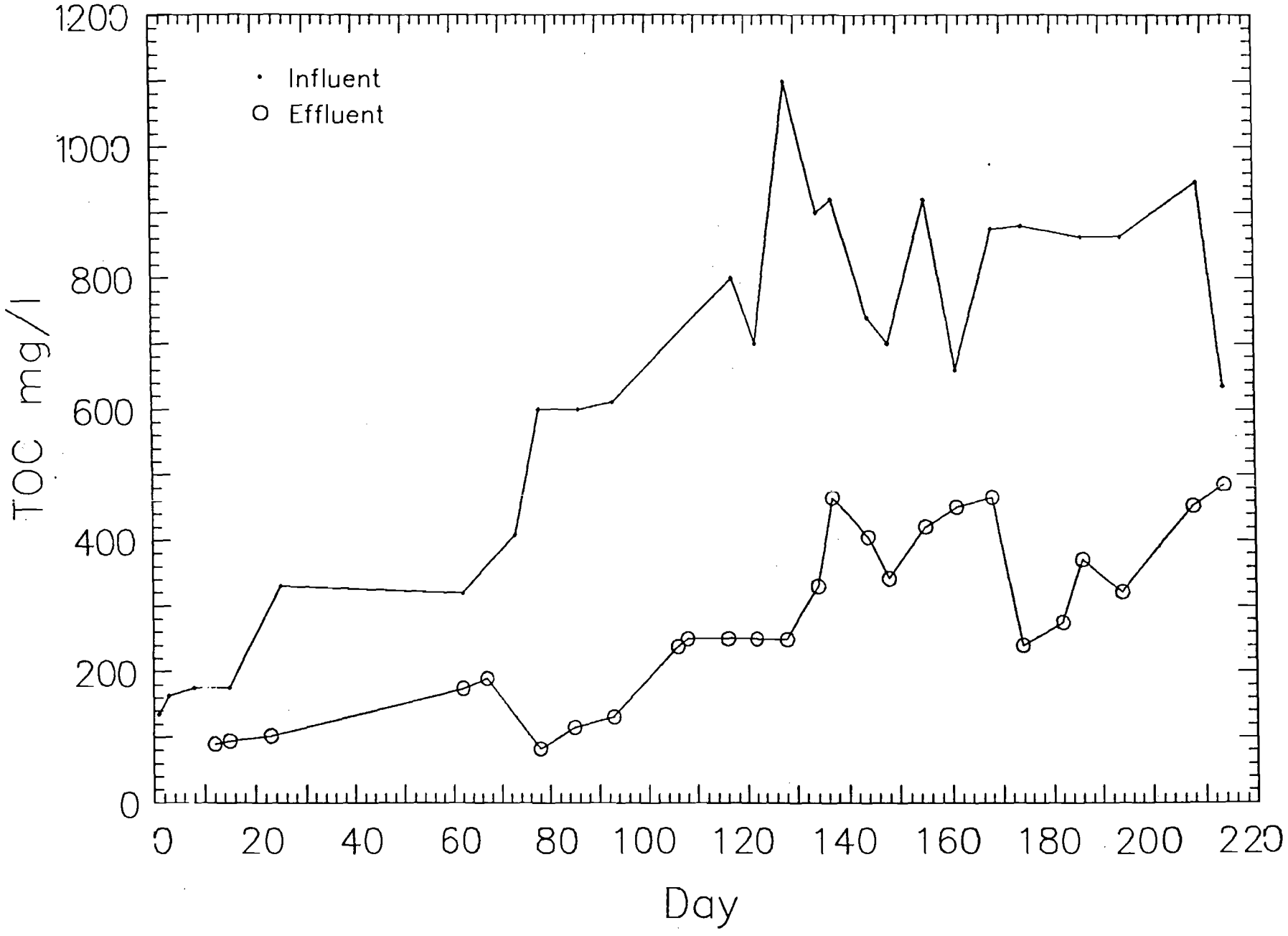

Fig. 35 Total Organic Carbon Removal in an Anaerobic Fluidized Activated Carbon Filter Using Pretreated Wastewater as Feed.

HYDANTOIN ADSORPTION STUDIES

Pretreated Wastewater

A solvent extracted-steam stripped wastewater was furnished by UNDERC for use in a treatability study. This wastewater has most of the TOC and NH_3 removed by the solvent-extraction-steam stripping process. The major constituents remaining are the highly water soluble hydantoins and traces of other organic constituents. Table 3 gives the major constituents found in the pretreated wastewater.

Studies using anaerobic activated carbon filters for the removal of hydantoins did not lead to a successful biological removal system. Therefore, studies were initiated to investigate the feasibility of 1) utilizing physical adsorption of the hydantoins onto the granular activated carbon to remove them from solution and 2) regenerate the exhausted carbon by use of a solvent. Initially, pure compound studies were carried out using the two most predominant hydantoin in the pretreated wastewater, 5-ethyl-5-methyl hydantoin and 5,5-dimethyl hydantoin. In addition, data was obtained on the adsorption of the parent compound, hydantoin.

Batch Kinetic Tests. The results of the single solute batch kinetics tests are shown in Figures 36, 37, and 38. The initial experimental conditions are shown in Table 14.

The batch tests were performed by preparing 4 L of an aqueous solution of one of the compounds, placing the solution in a constant temperature room, stirring the solution at a fixed rpm and then adding a known mass of carbon (Calgon, Filtrasorb 400) to the solution. Periodically, aliquots of the solution were removed from the reactor and filtered or centrifuged to remove the suspended carbon. The resulting filtrate or centrifugate was then quantitatively analyzed for the target compound.

The batch kinetic study for hydantoin had a C_o value of 450 mg/L which decreased to 395 mg/L, the equilibrium concentration, in a 1.5 hour time period. Eighty-five percent of the adsorption by the activated carbon occurred in the first 20 minutes of the experiment. The same basic sequence occurred for the other two solutes. The batch kinetic tests for 5,5-dimethylhydantoin with a C_o of 500 mg/L reach equilibrium concentration after 3 hours, as did the 5-ethyl-5-methylhydantoin with the same initial concentration. Most of the adsorption of both solutes also occurred in the first 20 minutes of the test.

From the batch kinetic test results, it can be concluded that the adsorption of the hydantoins was very rapid. Equilibrium was definitely reached after 3 hours for each compound and, therefore, three hours would be the minimum elapsed time required to ensure that equilibrium concentration is reached.

Isotherm Tests. The results of the isotherm tests are shown in Figures 39, 40, and 41. The initial experimental conditions are shown in Table 15.

The isotherms for hydantoin and 5,5-dimethylhydantoin were very similar with the only difference being a slight increase in curvature for the 5,5-dimethylhydantoin isotherm over the hydantoin with equilibrium concentrations in excess of 10 mg/L. The mass of solute adsorbed per mass of carbon (X/m) values for a given equilibrium concentration were also very similar.

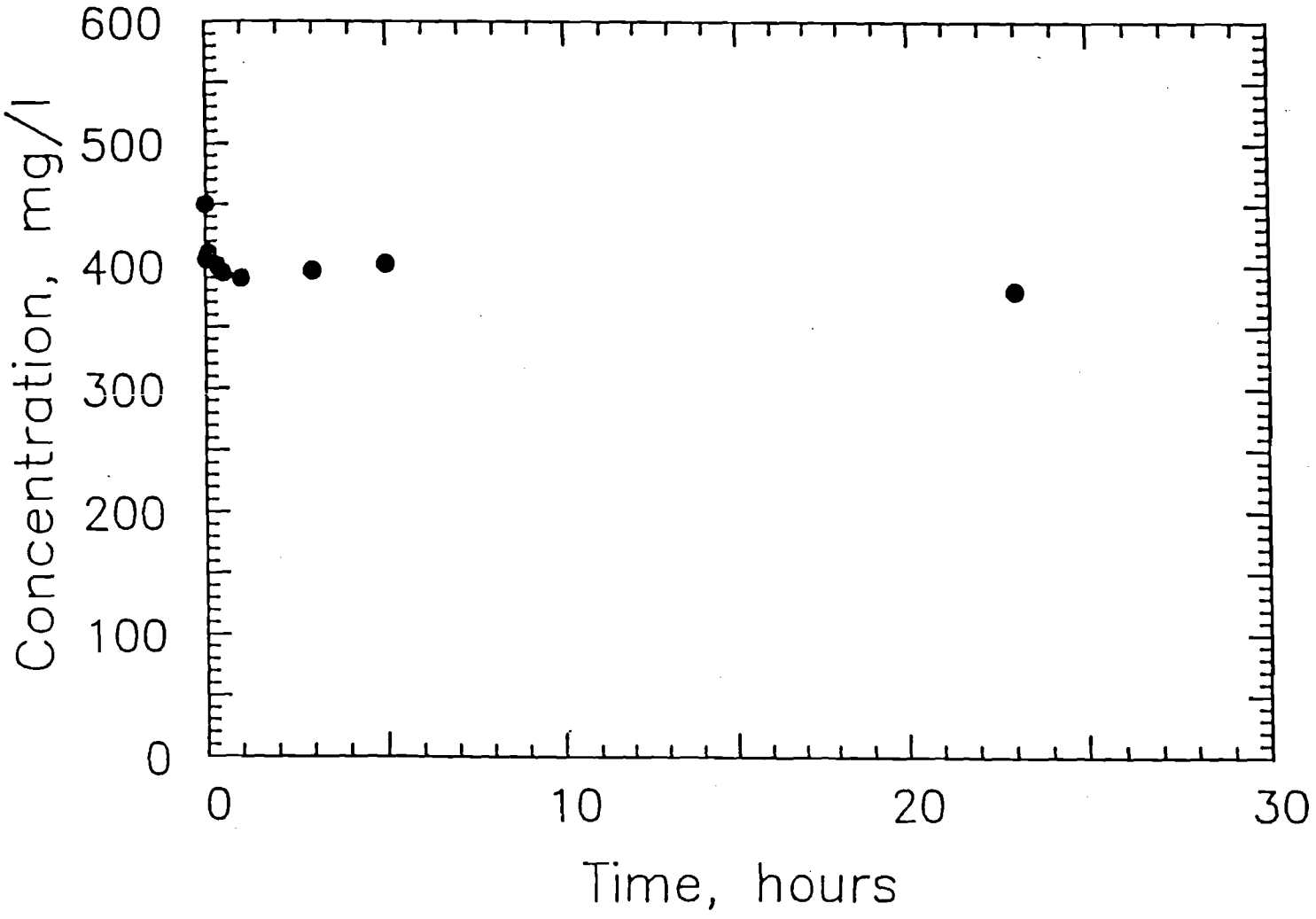

Fig. 36 Batch Kinetic Curve - Hydantoin Adsorbed on Filtrasrob 400.

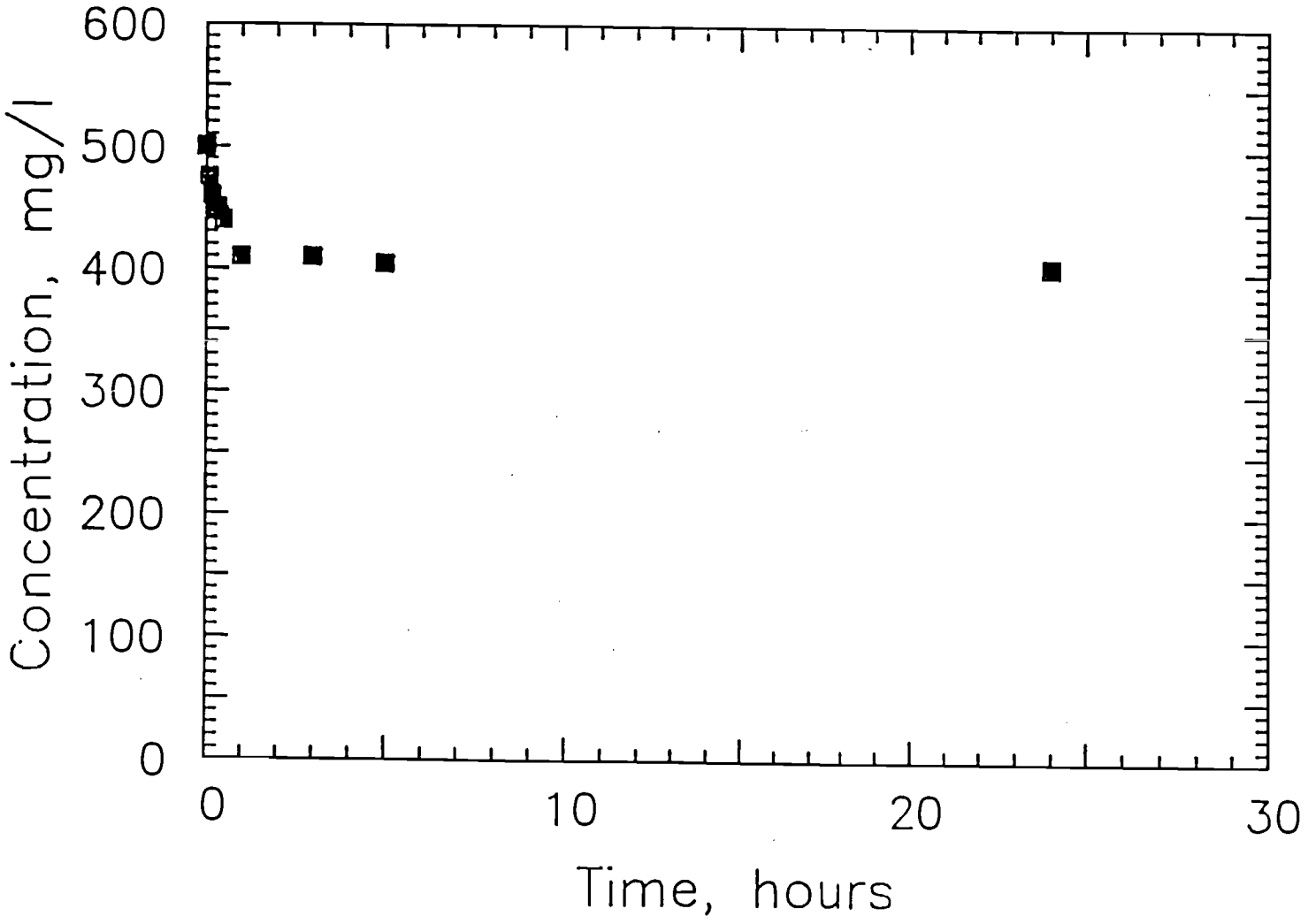

Fig. 37 Batch Kinetic Curve - 5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

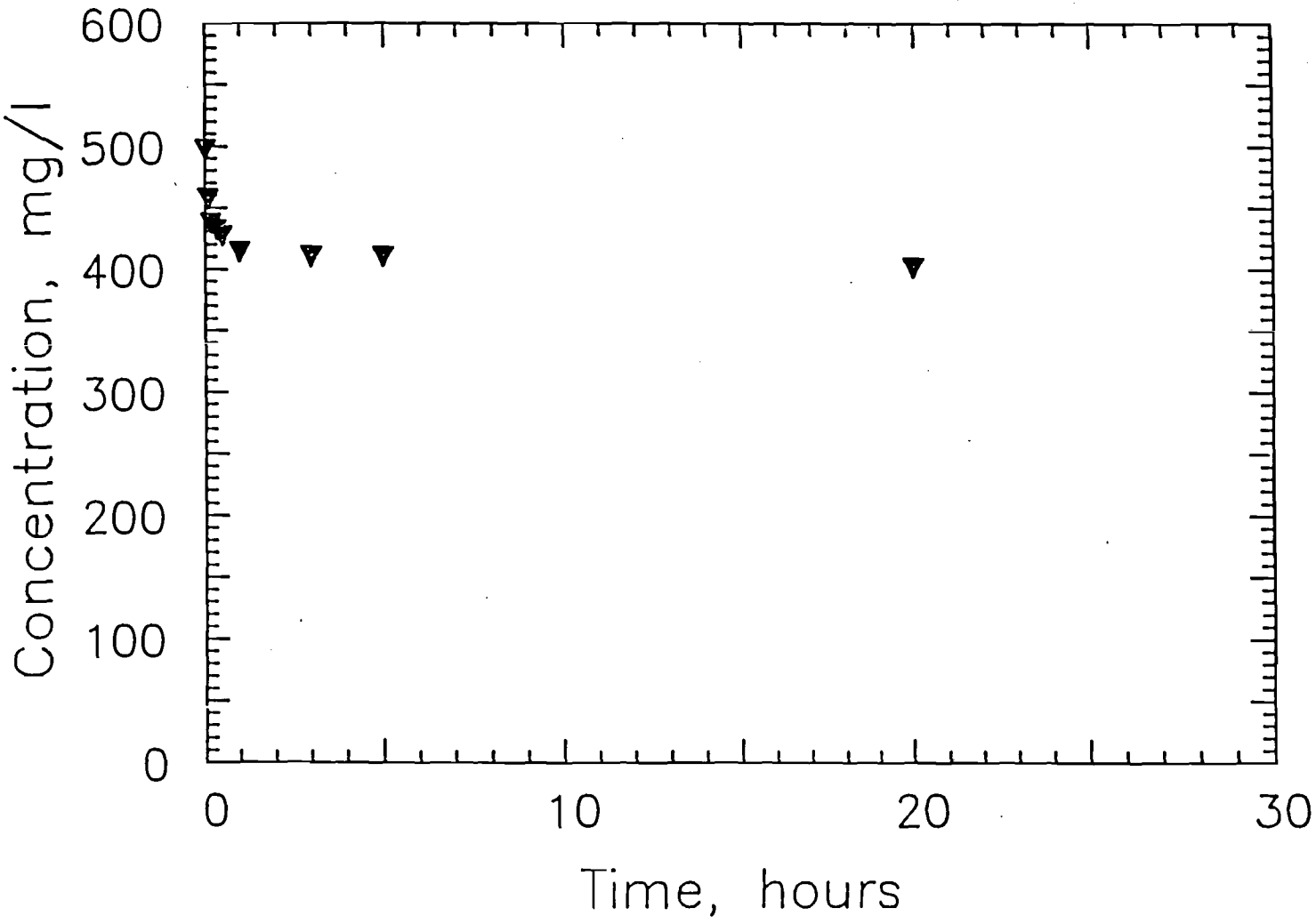

Fig. 38 Batch Kinetic Curve - 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 14. Initial Experimental Conditions - Adsorption Batch Kinetic Tests

hydantoin		
temperature		24°C
C_o		450 mg/L
carbon, Filtrasorb 400,	60x80 Mesh	0.75 g/L
stirrer speed		800 rpm
adsorbate volume		4.0 L
pH		approx. 5.2
5,5-dimethylhydantoin		
temperature		24°C
C_o		500 mg/L
carbon, Filtrasorb 400,	60x80 Mesh	0.75 g/L
stirrer speed		800 rpm
adsorbate volume		4.0 L
pH		approx. 5.2
5-ethyl-5-methylhydantoin		
temperature		25°C
C_o		500 mg/L
carbon, Filtrasorb 400,	60x80 Mesh	0.75 g/L
stirrer speed		800 rpm
adsorbate volume		4.0 L
pH		approx. 5.2

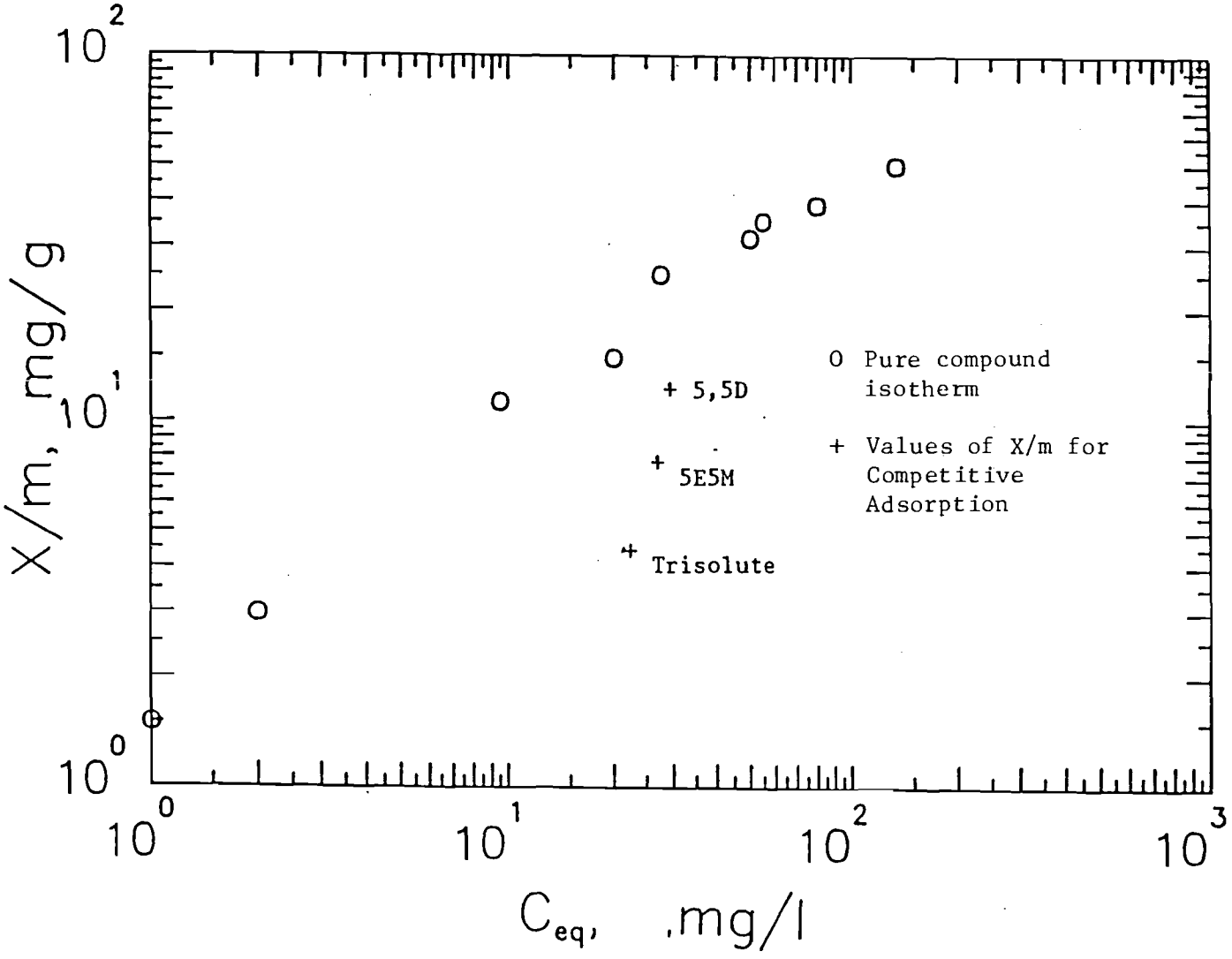

Fig. 39 Adsorption Isotherm - Hydantoin on Filtrasorb 400.

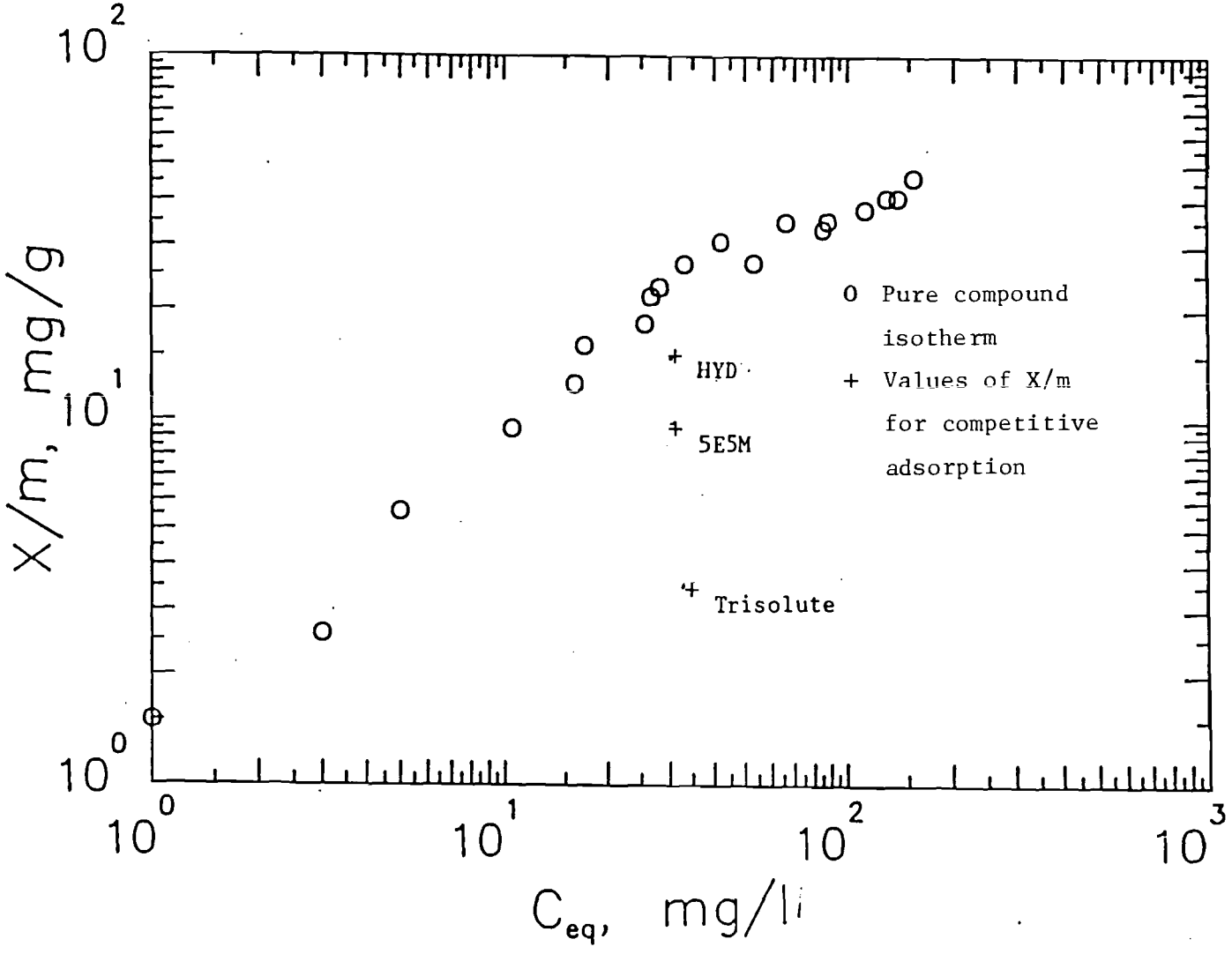

Fig. 40 Adsorption Isotherm - 5,5-Dimethylhydantoin on Filtrasorb 400.

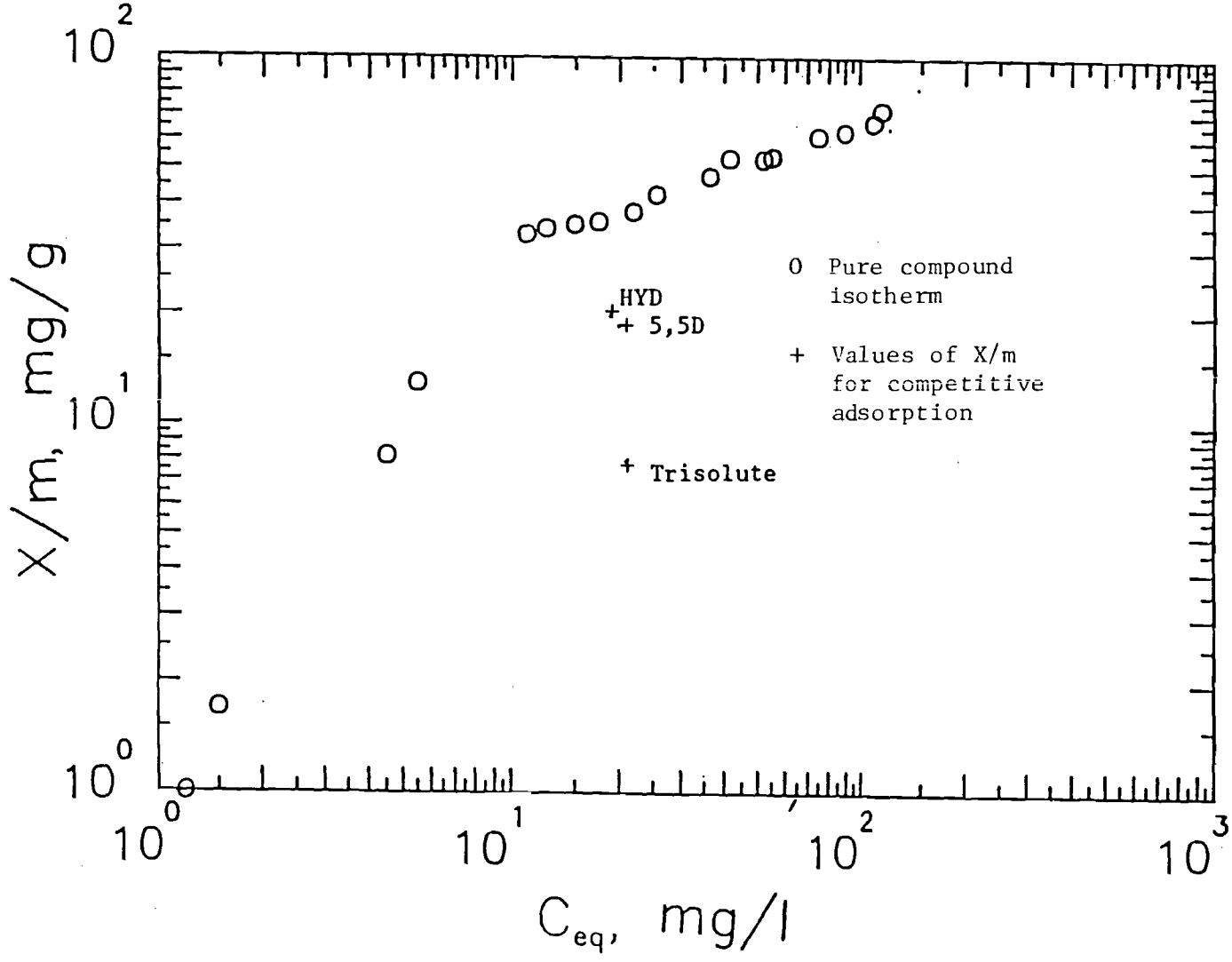

Fig. 41 Adsorption Isotherm - 5-Methyl-5-Ethylhydantoin on Filtrasorb 400.

Table 15. Initial Experimental Conditions for Isotherm Tests

Single solute adsorption	
temperature	28°C
C_o	various
carbon, Filtrasorb 400, 60x80 Mesh	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2
Bisolute competitive adsorption	
temperature	28°C
C_o	50 mg/L each
carbon, Filtrasorb 400, 60x80 Mesh	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2
Trisolute competitive adsorption	
temperature	28°C
C_o	50 mg/L each
carbon, Filtrasorb 400, 60x80 Mesh	2.5 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2

The isotherm for 5-ethyl-5-methylhydantoin was much different from the other two solutes. The isotherm, when plotted in a log-log mode, showed a distinct change in slope with increasing C_{eq} values. The change in slope occurred at a C_{eq} value of 12 mg/L and an X/m value of 35. Overall, there was a higher X/m value for any given equilibrium concentration indicating an adsorption preference for 5-ethyl-5-methylhydantoin over the other solutes. In examining all three curves as a whole, there appears to be a systematic transition in curvature in concentrations in excess of 10 mg/L from hydantoin to 5-ethyl-5-methylhydantoin. Also shown are the results of the bisolute and trisolute isotherm points. Each point represents the X/m and equilibrium concentration found for a given solute in competition with the labelled solute. For instance, in Figure 39, which is the isotherm for hydantoin, the point labelled 5,5 D represents the X/m value found for hydantoin in the bisolute hydantoin/5,5-dimethylhydantoin isotherm point. The point labelled trisolute represents the X/m value for hydantoin in the trisolute isotherm point. As can be expected, competition tends to reduce the amount of adsorbate adsorbed for a given equilibrium concentration. The relative affinity for the various solutes is also indicated by the fact that less hydantoin was adsorbed when in competition with 5-ethyl-5-methylhydantoin than when in competition with 5,5-dimethylhydantoin. When in competition with two different solutes, the amount adsorbed is even less. Since there are only a finite number of adsorption sites available, it was reasonable to assume that the increased competition between solutes in the trisolute isotherm point caused less of the individual solutes to be adsorbed than would be the case for the single or bisolute isotherm point.

In comparing each of the bisolute isotherm points, it appears that the relative affinity of activated carbon is in the order of hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin.

The curvature found in the adsorption isotherms represents a departure from the strict Freundlich equation at equilibrium concentrations over approximately 10 mg/L. Therefore, some of the assumptions on which the Freundlich equation are based are invalid for the case in hand. Such assumptions were: 1) exponential distribution of adsorption energies; 2) one adsorbate molecule per adsorption site; 3) no surface transmigration of solute molecules; and, 4) monolayer adsorption. The three assumptions may or may not be valid, but it is probable that monolayer adsorption was still occurring at the highest equilibrium concentration tested.

pH Tests. The results of the high, medium, and low isotherm points with pH adjusted to values of 4, 7, and 9 are shown in Figures 42, 43, and 44. The initial conditions for each of the three solutes are shown in Table 16.

The isotherm points with pH adjusted to 4 and 7 provided equal X/m values for all three solutes at the medium and high concentration points. The variation in X/m values at the low isotherm points were small and probably due to experimental error. Of consequence were the X/m values of the isotherm points with the pH adjusted to 9. These points have X/m values significantly lower than the single solute curve and the X/m values at pH 4 and 7. Therefore, less solute is adsorbed at pH 9 than at a pH of 4 or 7.

Column Studies. The initial conditions for the column studies are shown in Table 17.

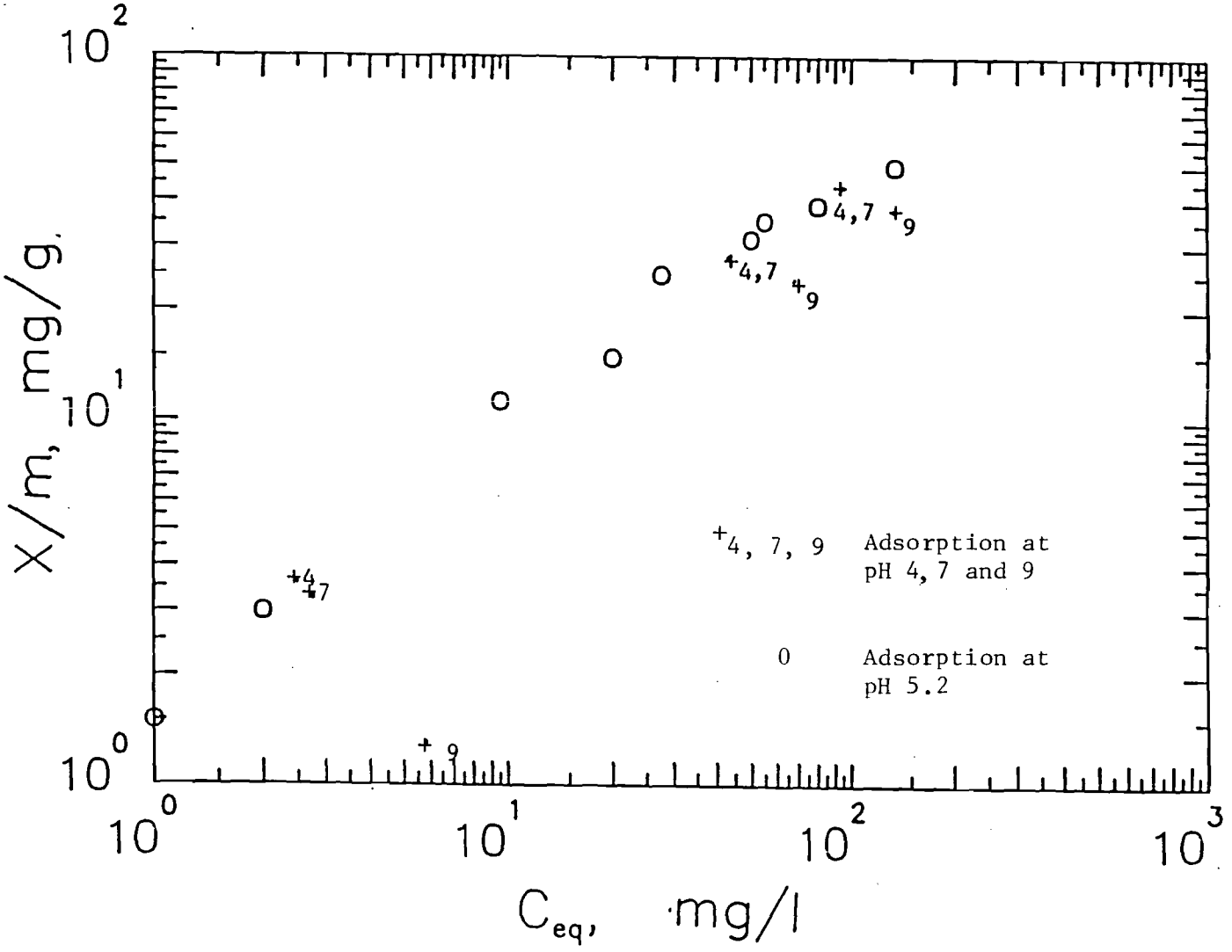

Fig. 42 Isotherm - pH Plot - Hydantoin Adsorbed on Filtrasorb 400.

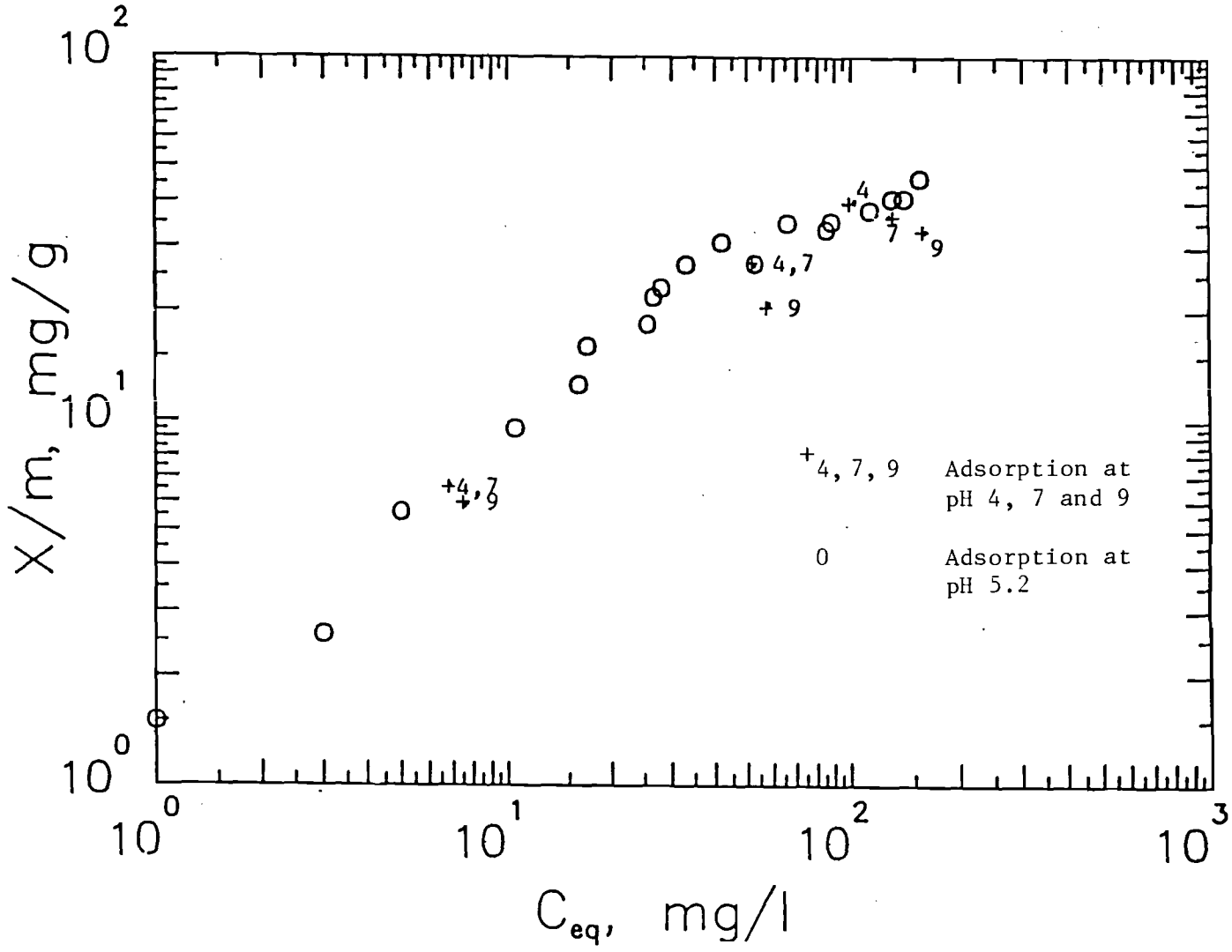

Fig. 43 Isotherm - pH Plot - 5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

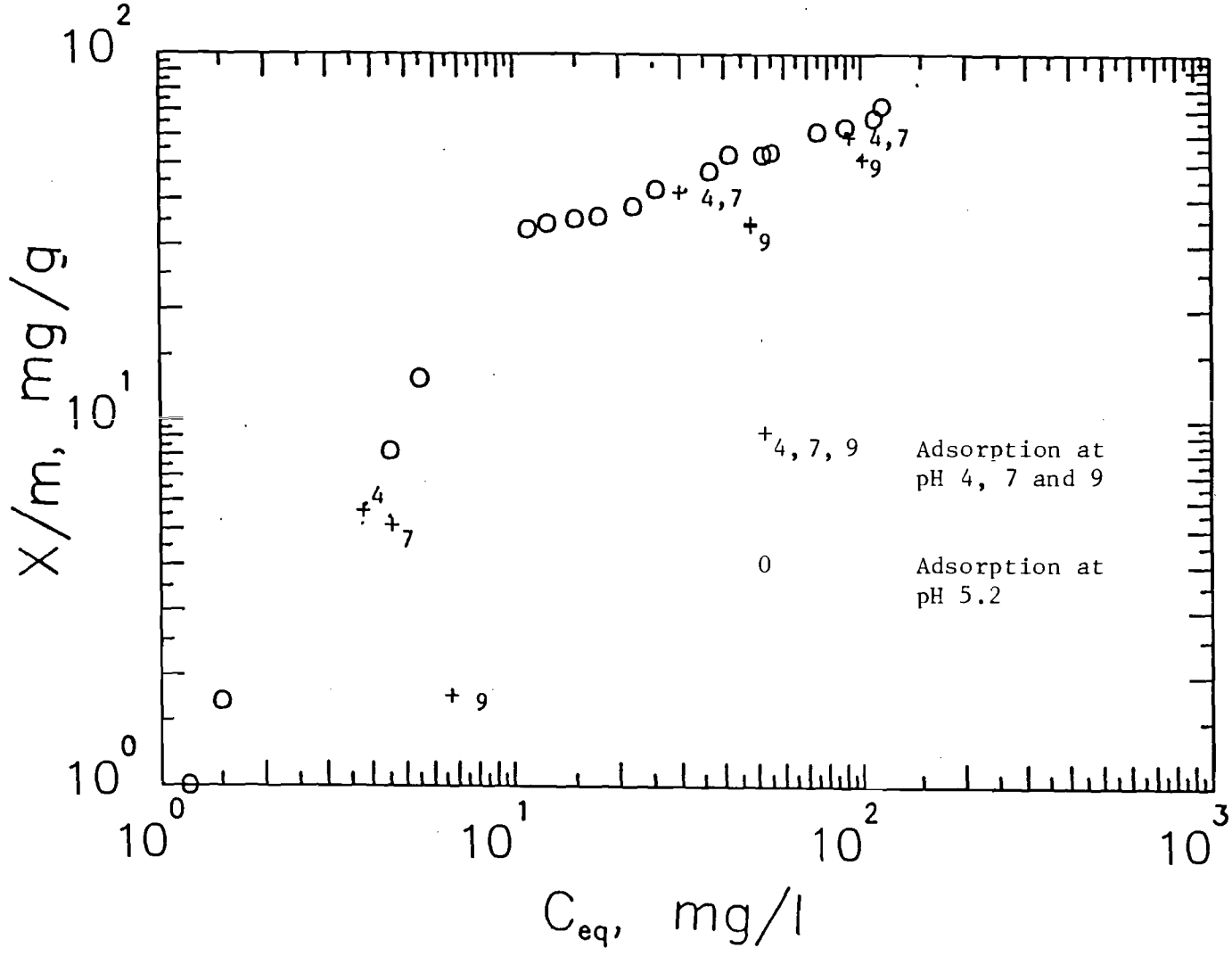

Fig. 44 Isotherm - pH Plot - 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 16. Initial Experimental Conditions for Adsorption Tests at Various pH Values

Temperature	28°C
C_o	50 mg/L
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	4, 7, 9

Table 17. Initial Experimental Conditions for Continuous Flow Adsorption Studies

hydantoin		
	temperature	28°C
	influent concentration	55 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
5,5-dimethylhydantoin		
	temperature	28°C
	influent concentration	45 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
5-ethyl-5-methylhydantoin		
	temperature	28°C
	influent concentration	50.5 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
hydantoin/5,5-dimethylhydantoin		
	temperature	28°C
	influent hydantoin	40 mg/L
	5,5-dimethylhydantoin	59 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
hydantoin/5-ethyl-5-methylhydantoin		
	temperature	28°C
	influent hydantoin	30.9 mg/L
	5-ethyl-5-methylhydantoin	50 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin		
	temperature	27°C
	influent 5,5-dimethylhydantoin	49.5 mg/L
	5-ethyl-5-methylhydantoin	54 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
trisolute		
	temperature	27°C
	influent hydantoin	41.5 mg/L
	5,5-dimethylhydantoin	38 mg/L
	5-ethyl-5-methylhydantoin	33 mg/L
	flow rate	20 mL/min
	carbon	3.75 g
	pH	5.6
coal gasification wastewater		
	temperature	28°C
	influent	undiluted
	flow rate	100 mL/min
	carbon	30.0 g
	pH	8.76

The results of the single solute column studies are depicted in Figures 45, 46, and 47. To provide a meaningful basis for comparison of the relative adsorption preferences of the three solutes, a calculation of the X/m values, Table 18, (amount of solute adsorbed per unit weight of carbon) reveals the following:

The X/m value for hydantoin is slightly higher than expected. However, if the X/m value of 41 mg/g with a C_{eq} of 55 mg/L is plotted on the single solute isotherm for hydantoin (Figure 39), it will be seen to be within experimental error. The X/m values for the other two solutes plot directly on the single solute curves (Figures 40 and 41). From the single solute column studies, it is readily apparent that 5-ethyl-5-methylhydantoin is more strongly adsorbed than the other two adsorbents.

More vivid evidence for the various affinities of the carbon for the different solutes was provided by the bisolute and trisolute breakthrough curves which are shown in Figure 48, 49, 50 and 51. The calculated X/m values for the bisolute and trisolute breakthrough curves are shown in Table 19.

Although from Figure 41 it appeared that the affinity of the carbon for hydantoin and 5,5-dimethylhydantoin was equal, the X/m values for the hydantoin/5,5-dimethylhydantoin in Table 19 showed that the carbon had a higher capacity for 5,5-dimethylhydantoin over hydantoin. The bisolute curve hydantoin/5-ethyl-5-methyl-hydantoin (Figure 49) showed a stronger adsorption of 5-ethyl-5-methylhydantoin by the fact that hydantoin was displaced from the activated carbon during the column test. This was demonstrated by the effluent concentration of the hydantoin becoming greater than the influent concentration. This was caused by all hydantoin in the influent passing through the column unadsorbed, and additional hydantoin was added to the effluent due to displacement from the carbon through competition with the more strongly adsorbed 5-ethyl-5-methylhydantoin. A comparison of the X/m values in Table 19 also showed that 5-ethyl-5-methylhydantoin was more strongly adsorbed than hydantoin. The bisolute curve 5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin again showed a displacement of the more weakly adsorbed solute, 5,5-dimethylhydantoin, by the more strongly adsorbed 5-ethyl-5-methyl-hydantoin. The X/m values in Table 19 verify that the carbon has a higher adsorption capacity for the 5-ethyl-5-methylhydantoin over the 5,5-dimethyl-hydantoin.

A double displacement effect occurred in the trisolute breakthrough curve. The most strongly adsorbed 5-ethyl-5-methylhydantoin displaced both hydantoin and 5,5-dimethylhydantoin from the carbon as can be see in Figure 51. From Table 19, the X/m values for hydantoin and 5,5-dimethylhydantoin were equal while the carbon exhibited a much higher adsorption capacity for the 5-ethyl-5-methylhydantoin.

Overall, a review of the results in Table 19 show an adsorption preference of 5-ethyl-5-methylhydantoin > 5,5-dimethylhydantoin > hydantoin.

The breakthrough curves for two of the hydantoins and phenol in the actual pretreated coal gasification effluent is shown in Figure 52. Immediately following is the breakthrough curve for total organic carbon for the wastewater, Figure 53. The amount of carbon used in the column was 30 grams with a flow rate of 100 mL/min. From Figure 52, the least strongly

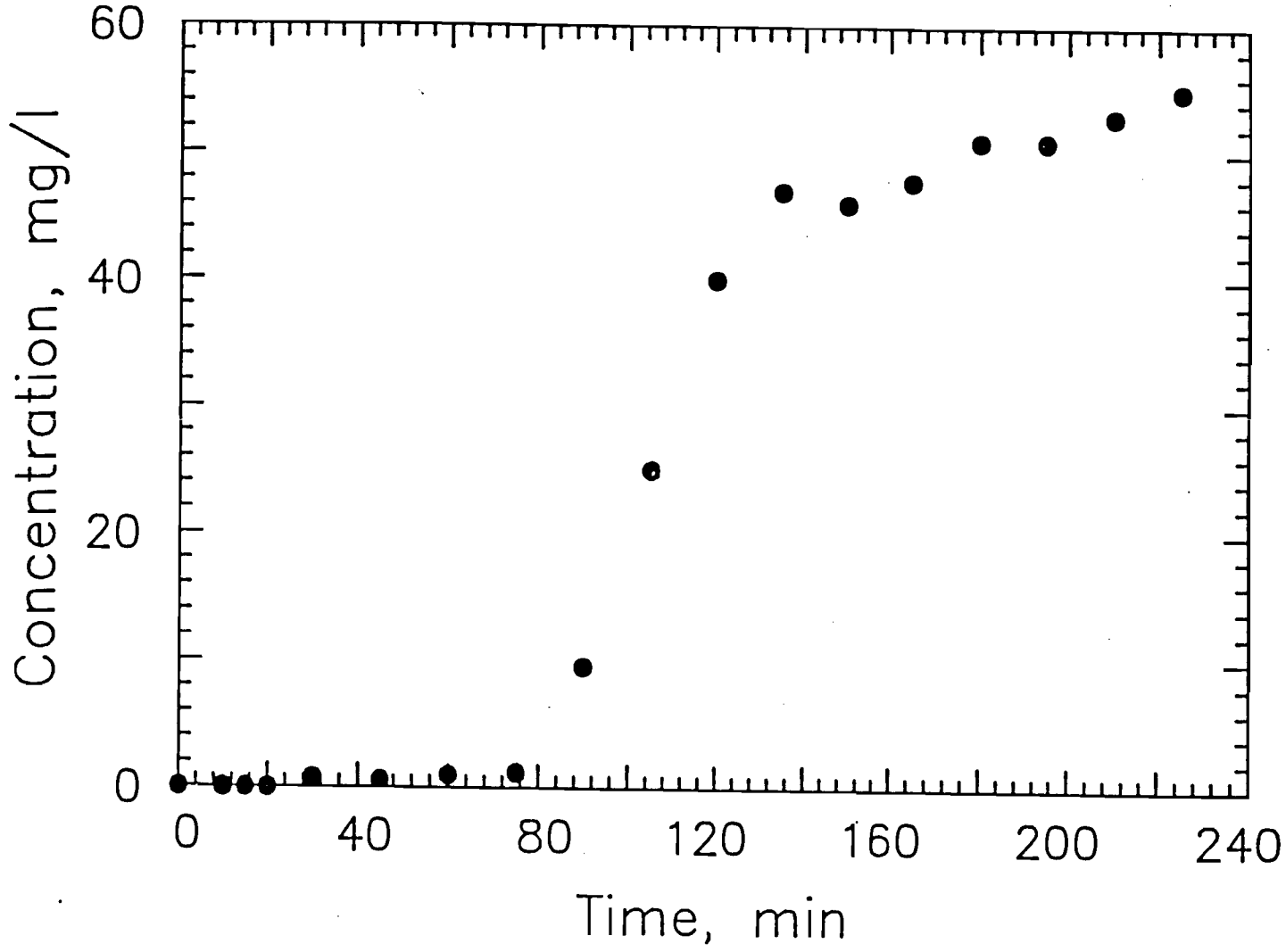

Fig. 45 Column Breakthrough Curve - Hydantoin Adsorbed on Filtrasorb 400.

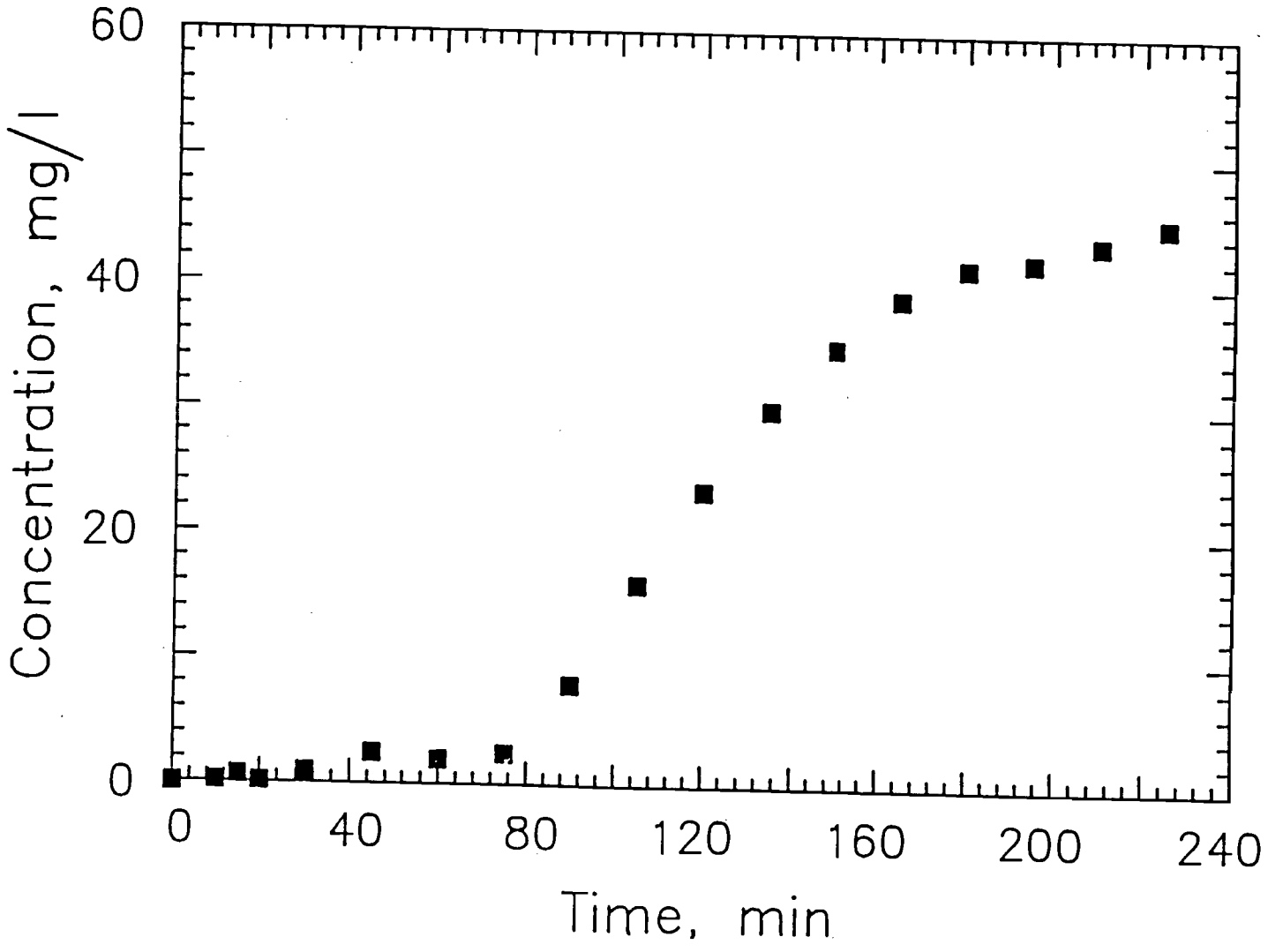

Fig. 46 Column Breakthrough Curve - 5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

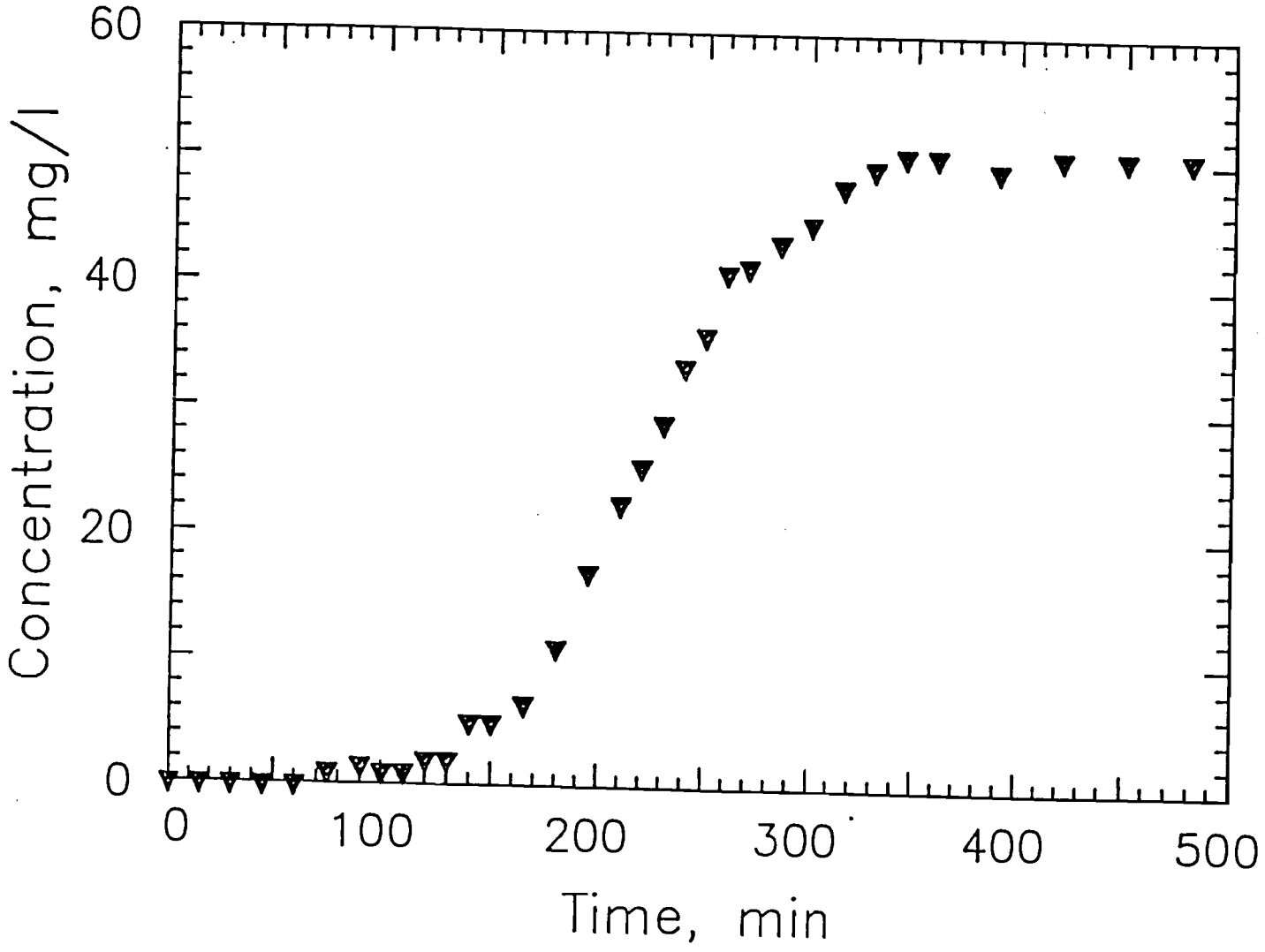

Fig. 47 Column Breakthrough Curve - 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 18. Single Solute X/m Values for Continuous Flow Column Adsorption Studies

hydantoin	43 mg/g
5,5-dimethylhydantoin	31 mg/g
5-ethyl-5-methylhydantoin	61 mg/g

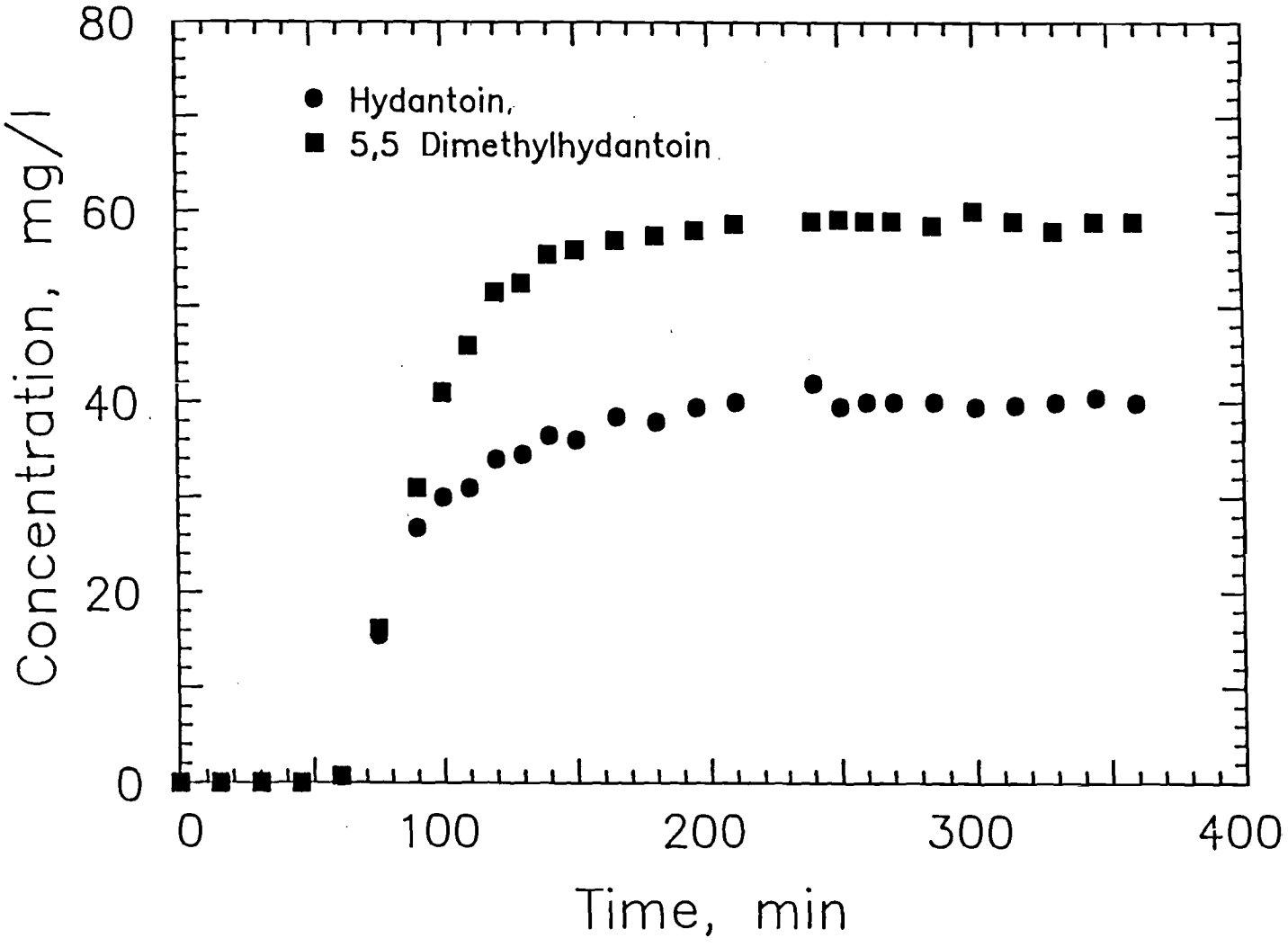

Fig. 48 Bisolute Breakthrough Curve - Hydantoin/5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

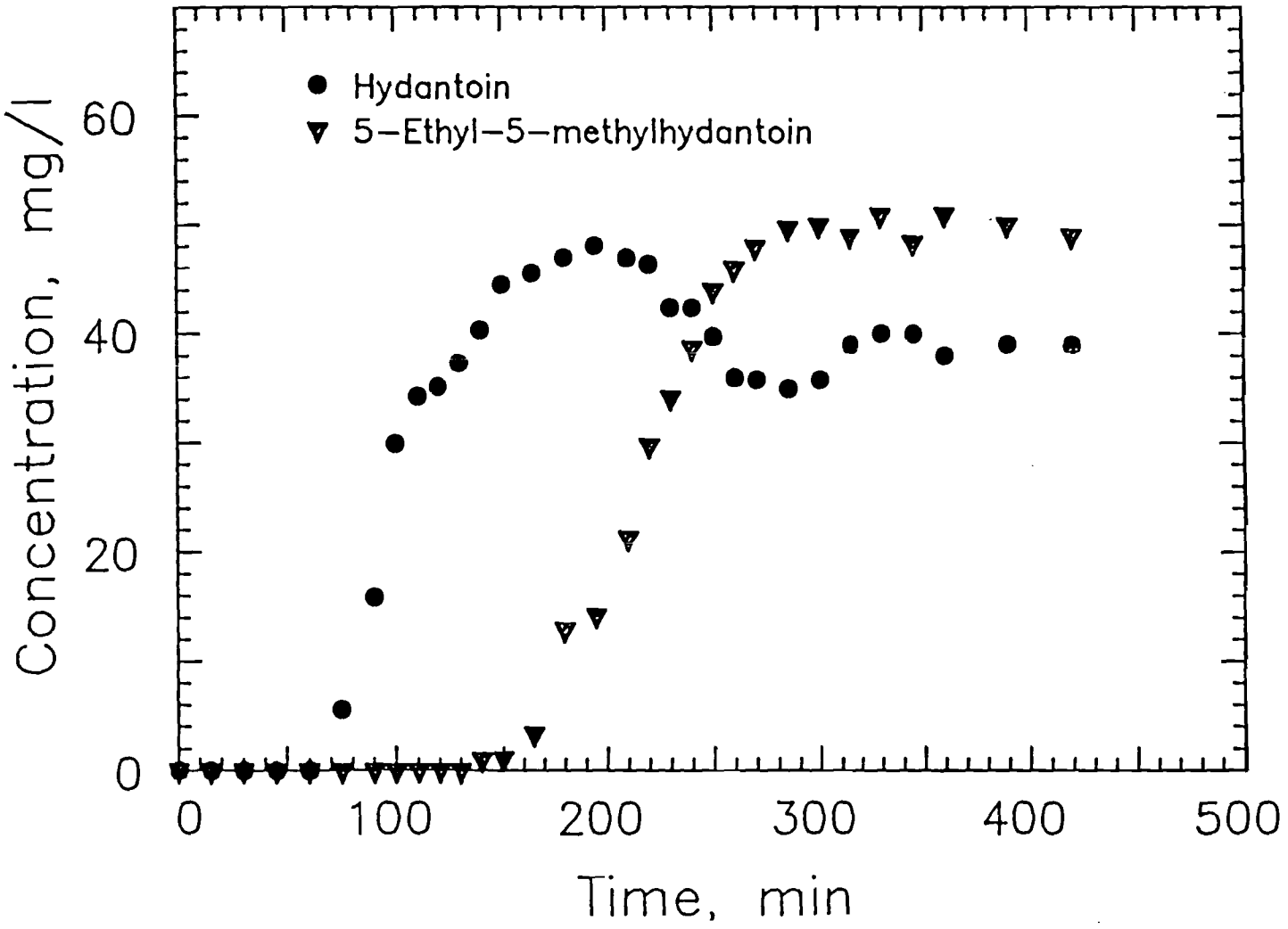

Fig. 49 Bisolute Breakthrough Curve - Hydantoin/5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

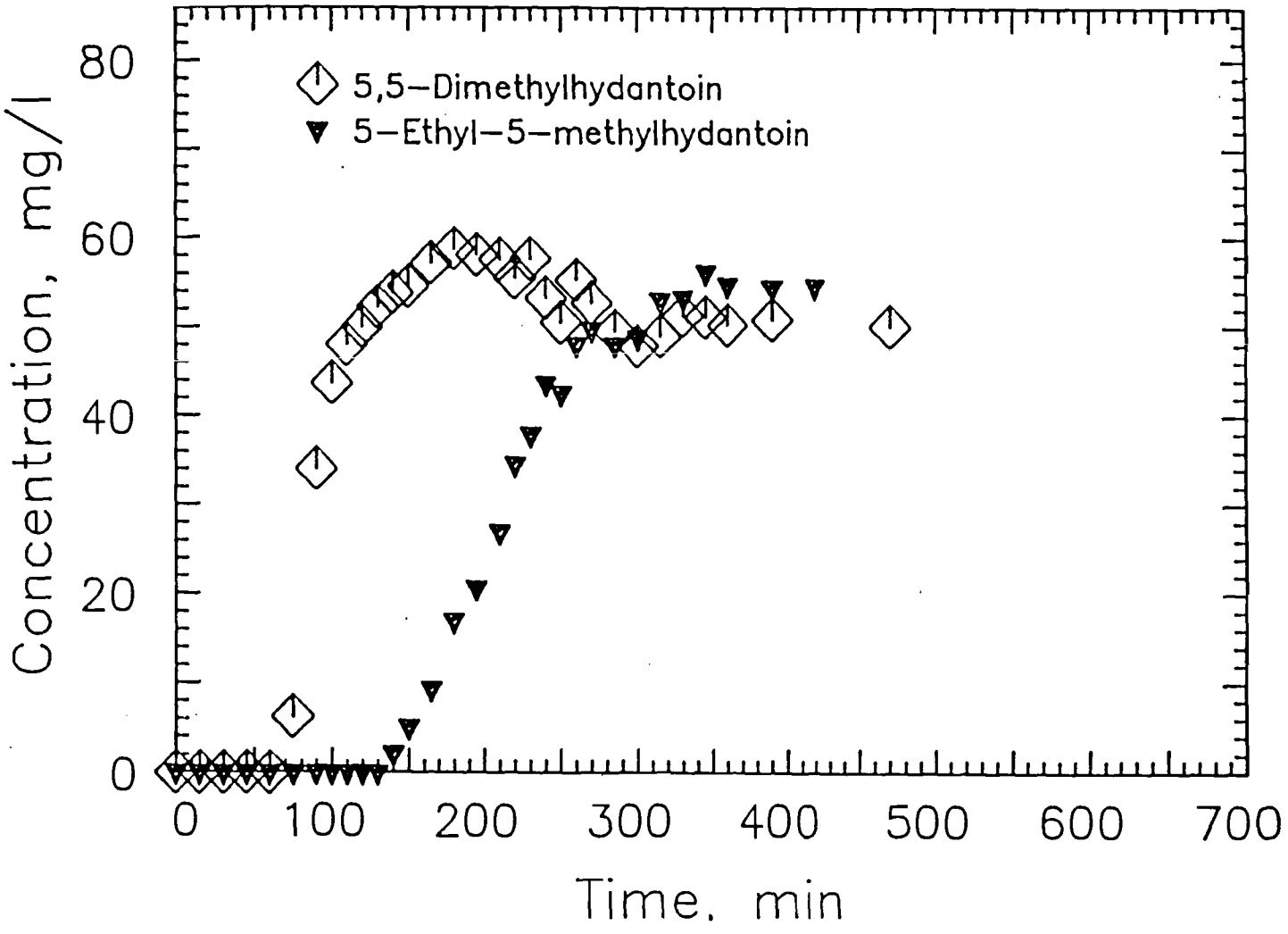

Fig. 50 Bisolute Breakthrough Curve - 5,5-Dimethylhydantoin/5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

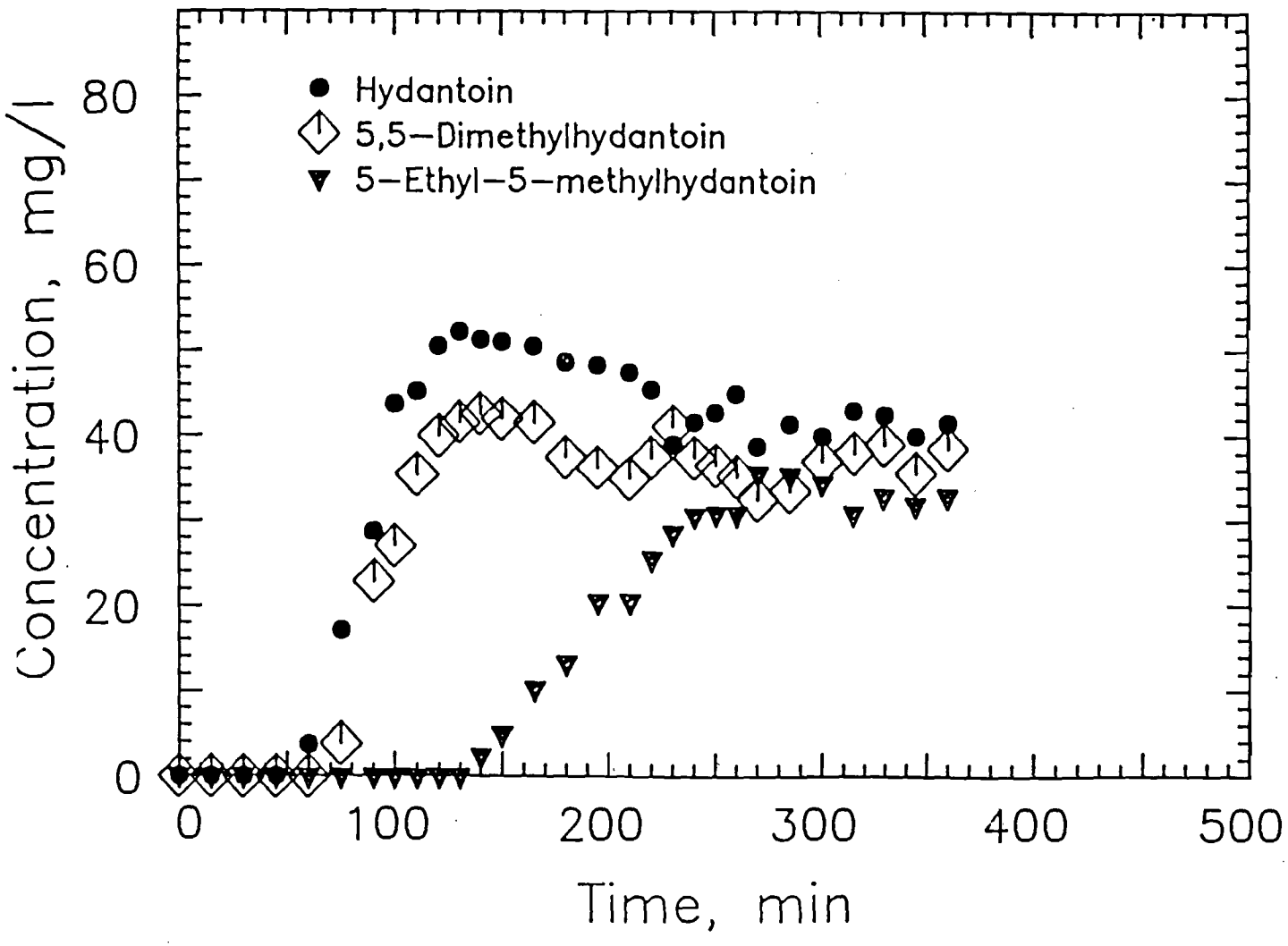

Fig. 51 Trisolute Breakthrough Curve Hydantoin, 5,5-Dimethylhydantoin, 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 19. Bisolute and Trisolute X/m Values for Continuous Flow Column Adsorption Studies

hydantoin/5,5-dimethylhydantoin	
hydantoin	21 mg/g
5,5-dimethylhydantoin	36 mg/g
hydantoin/5-ethyl-5-methylhydantoin	
hydantoin	19 mg/g
5-ethyl-5-methylhydantoin	57 mg/g
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin	
5,5-dimethylhydantoin	22 mg/g
5-ethyl-5-methylhydantoin	58 mg/g
trisolute	
hydantoin	17 mg/g
5,5-dimethylhydantoin	17 mg/g
5-ethyl-5-methylhydantoin	33 mg/g

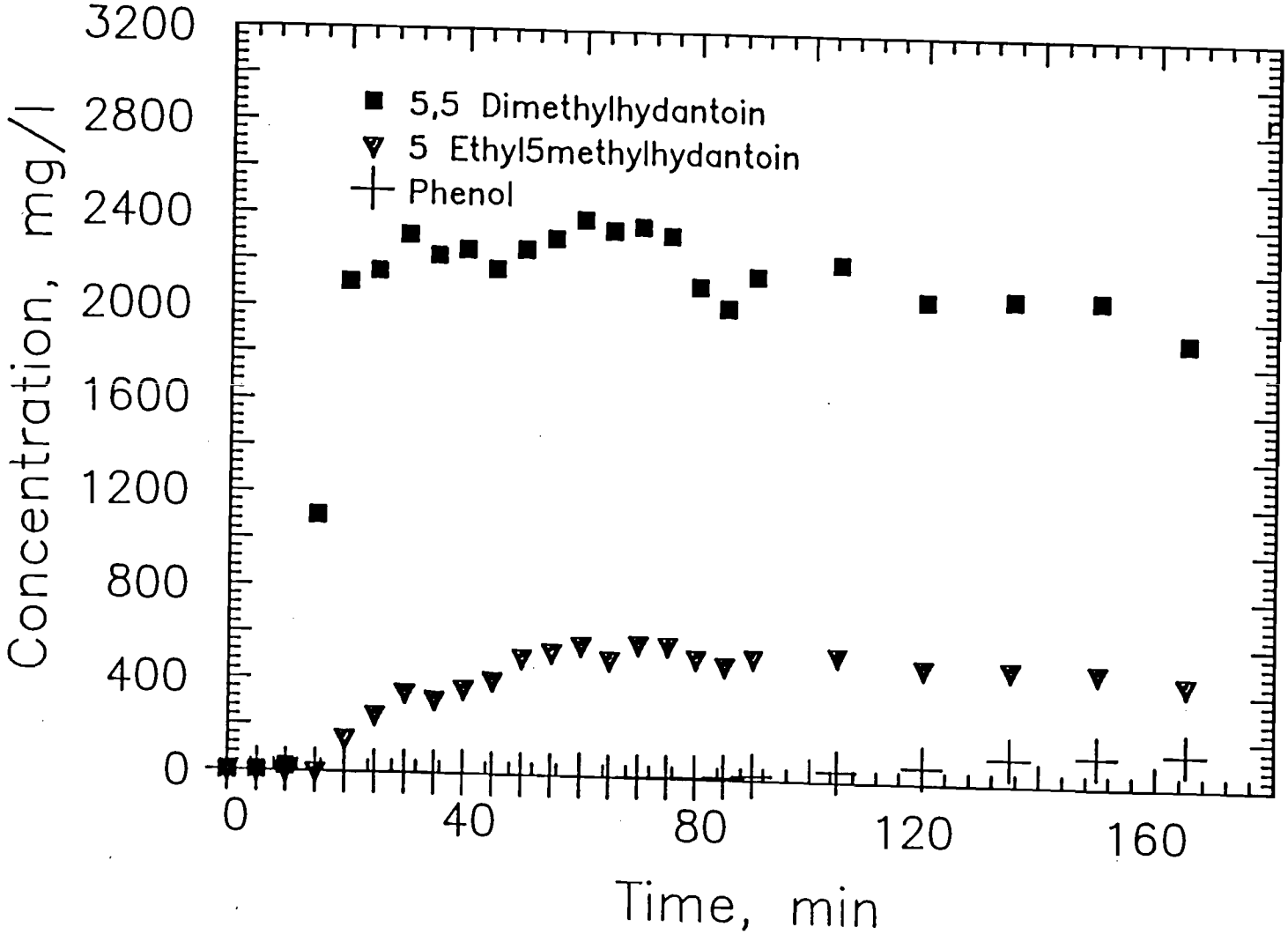

Fig. 52 Breakthrough Curve - Pretreated Coal Gasification Effluent Adsorbed on Filtrasorb 400.

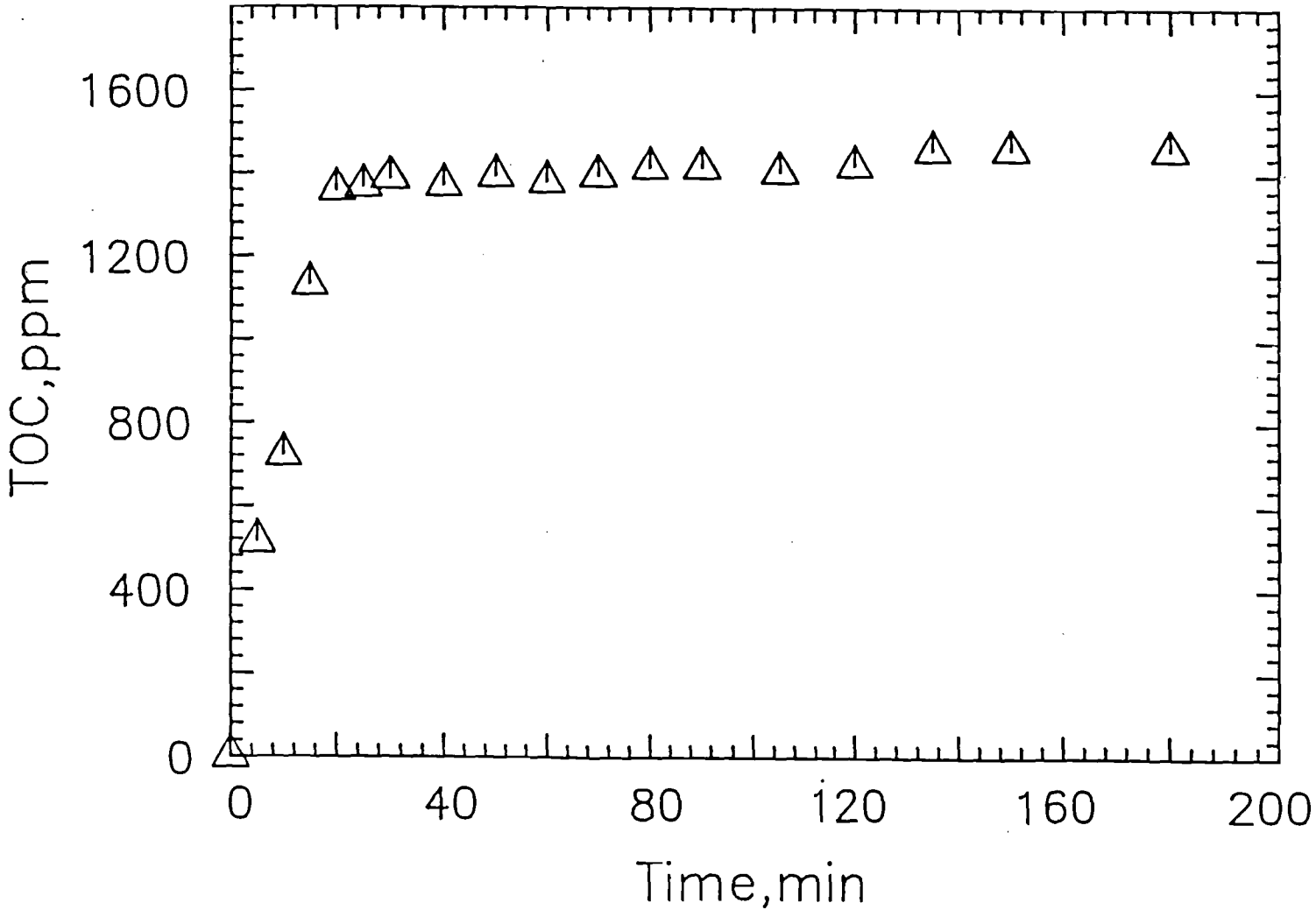

Fig. 53 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent Adsorbed on Filtrasorb 400.

adsorbed 5,5-dimethylhydantoin broke through first between 10 and 15 minutes from the start of the test followed by 5-ethyl-5-methylhydantoin breakthrough between 15 and 20 minutes. 5,5-Dimethylhydantoin reached carbon exhaustion at 1977 mg/L within 10 minutes of initiating breakthrough. 5-Ethyl-5-methylhydantoin reached influent concentration after 55 minutes. Phenol did not appear in the effluent until 85 minutes from the test start and slowly reached exhaustion at 165 minutes. A slight displacement of solute occurred with 5,5-dimethylhydantoin being displaced by the 5-ethyl-5-methylhydantoin. Also, slight displacement of the 5-ethyl-5-methylhydantoin by the phenol occurred.

The X/m values for each of the solutes measured in the pretreated coal gasification effluent are shown in Table 20.

At face value, it appears that 5,5-dimethylhydantoin was more strongly adsorbed than phenol in the coal gasification wastewater due to its higher X/m value in Table 20. However, the higher X/m value is due to the concentration of the 5,5-dimethylhydantoin being an order of magnitude higher than the phenol concentration. A more definitive determination of adsorption preferences can be obtained from the coal gasification wastewater breakthrough curves where phenol was the last compound to be observed in the column effluent, and where phenol displaced both 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin from the carbon. Phenol was apparently the most strongly adsorbed compound.

A comparison of the X/m values found in Table 20 with the single solute isotherm curves for 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin (Figures 40 and 41) reveals that the X/m values found in the column study for coal gasification wastewater were significantly lower than the expected X/m values for the pure single solute system given equivalent solute concentrations. A comparison of X/m values for pure solute and actual wastewater is given in Table 21.

The TOC breakthrough curve is interesting since it shows that the wastewater contains some substances that are apparently not readily adsorbed on activated carbon. This is shown by noting that some TOC broke through the carbon column immediately from the start of the test. It is assumed that the compounds that were not adsorbed were large molecules that could not physically fit inside the carbon pore.

CONCLUSIONS

The batch kinetic tests for single solutes demonstrated that the kinetics of adsorption for hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin were very rapid with most of the adsorption occurring in the first 20 minutes.

The relative strength of adsorption of the three solutes was established by the single solute, bisolute, and trisolute isotherm points as follows: hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin. This relationship held true regardless of the relative concentration of each solute with respect to the other as demonstrated by the coal gasification wastewater breakthrough curve. Even though 5,5-dimethylhydantoin was present in concentrations of 1980 mg/L, 5-ethyl-5-methylhydantoin at concentrations of 460 mg/L

Table 20. Pretreated Coal Gasification Effluent X/m Values from Continuous Flow Column Adsorption Studies

5,5-dimethylhydantoin	96 mg/g
5-ethyl-5-methylhydantoin	42 mg/g
phenol	64 mg/g

Table 21. Comparison of X/m Values for Coal Gasification Wastewater and Pure Solutes

5,5-dimethylhydantoin		
	concentration in wastewater	1980 mg/L
	pure single solute X/m	145 mg/g
	wastewater X/m	96 mg/g
5-ethyl-5-methylhydantoin		
	concentration in wastewater	460 mg/L
	pure single solute X/m	120 mg/g
	wastewater X/m	42 mg/g

was still able to displace it from the carbon, and was therefore more strongly adsorbed. The bisolute and trisolute isotherm points also demonstrated competitive effects between the solutes relative to their respective strengths of adsorption. The X/m values for each adsorbate was markedly reduced by the presence of a second and third solute. Within a given weight of activated carbon, there was a finite number of adsorption sites that could be utilized by the three adsorbates. Although hydantoin was the least strongly adsorbed solute, it was not totally desorbed by either the 5,5-dimethylhydantoin or the 5-ethyl-5-methylhydantoin, and 5,5-dimethylhydantoin was not totally desorbed by the 5-ethyl-5-methylhydantoin. Since the X/m values for the less strongly adsorbed compounds are lower than the corresponding X/m value for the single solute, it is obvious some displacement of the weaker by the more strongly adsorbed compound occurs. However, since an apparently large percentage of the weaker adsorbate, hydantoin, would still be adsorbed on the carbon after the most strongly adsorbed compound, 5-ethyl-5-methylhydantoin, had reached equilibrium, adsorption sites on the carbon appear to have a site specific affinity for one particular solute over the other.

The characteristics of the various adsorbates could be the leading cause of the adsorption preferences encountered. The difference in molecular structure of the three solutes was the presence of the alkyl groups or hydrogen bonded to the C^5. Hydantoin had no alkyl groups and was the most weakly adsorbed. 5-Ethyl-5-methylhydantoin had the largest molecular weight function groups and was the most strongly adsorbed. 5,5-Dimethylhydantoin was in an intermediate position of adsorption strength. Examples of adsorption strength based upon functional groups attached to the solute molecules were previously found by Belfort[37].

The pH adjusted isotherm points within the high, mid-range, and low-range for each single solute isotherm conclusively showed that at a pH of 4 and 7, the X/m values were within experimental error of the isotherm curve. At pH 9, however, the X/m value was much lower. Therefore, at a pH of 9, the amount of solute adsorbed per unit weight of carbon is significantly reduced.

The X/m values for the single solute breakthrough curves were either directly on or within experimental error of the X/m value for an equivalent solute concentration on the pure solute breakthrough curves. This phenomena enhances the probability that the single solute isotherms are accurate.

For the bisolute and trisolute curves, the X/m values demonstrated the adsorption preference of the activated carbon for the three adsorbates. From Table 19, it is obvious that 5,5-dimethylhydantoin is more strongly adsorbed than hydantoin from the hydantoin/5,5-dimethylhydantoin X/m values, and from the trisolute X/m values, that 5-ethyl-5-methylhydantoin is more strongly adsorbed than both of the other two adsorbates. Also, by observing the solute displacements which occurred on the actual bisolute and trisolute breakthrough curves (Figures 48 through 51), a relative adsorption preference can be observed.

The pretreated coal gasification effluent breakthrough curves (Figure 52) with the associated X/m values (Table 20) yielded interesting results. A comparison of the X/m values for the coal gasification wastewater and pure solutes for equivalent solute concentrations (Table 20) showed significant reductions in the X/m values in the wastewater. The adsorption of

5,5-dimethylhydantoin was reduced by 34% and that of 5-ethyl-5-methylhydantoin was reduced 65% from the adsorption that would be expected in a pure solute system. The probable reasons for the reduction in adsorption capacity are twofold: (1) the increase in pH from 5.2 in pure systems to 8.76 in the actual wastewater, and (2) competition between the various solutes in the wastewater. From Figures 42, 43, and 44, it was shown that at a pH of 9, the amount of pure solute adsorbed on the carbon was reduced. Since the wastewater has a pH of 8.76, it is probable that the pH had an effect in reducing the X/m values for the wastewater. In addition, from the bisolute and trisolute isotherm points (Figures 42, 43, and 44) it was demonstrated that competition between the solutes will reduce the amount of hydantoins that will be adsorbed on activated carbon. In the coal gasification wastewater, the hydantoins were in competition with phenol (which was more strongly adsorbed) which would reduce the X/m values for the hydantoins. It is probable that both conditions contributed to a reduction in the amount of hydantoins adsorbed.

CARBON REGENERATION STUDY

If carbon adsorption were to be used as a method for removal of the hydantoins from the pretreated wastewater, a relatively inexpensive and rapid method of regeneration of the exhausted granular activated carbon would be desirable. Without a rapid and inexpensive regeneration scheme the use of carbon adsorption would not be economically viable due to the relative low capacity of the carbon for hydantoins.

Continuous flow carbon adsorption - solvent regeneration studies were carried out using 30 x 40 mesh Filtrasorb 400, pretreated (solvent extracted - steam stripped) wastewater and a series solvents. Flow rates were 5 mL/min and 2 mL/min for adsorption and regeneration, respectively. The results of the adsorption regeneration cycles are summarized in Table 22. Typical breakthrough and regeneration curves are given in Figures 54, 55, 56, and 57.

Regeneration values were calculated by determining the amount of compound adsorbed from the raw wastewater and the amount desorbed by the solvent. Regeneration was then defined as: $\frac{\text{amount desorbed}}{\text{amount adsorbed}} \times 100$.

CONCLUSIONS

Based on the quantity of carbon required for adsorption and the limited regeneration by the solvents used, it does not appear that this process is a viable one for the removal of hydantoins from the pretreated wastewater.

Table 22. Solvent Regeneration of Exhausted Activated Carbon

Solvent	% Capacity Regenerated
NaOH, 0.1 M	70
NaOH, 0.2 M	57,72*
HCl, 0.2 M	38
HCl, 1 M	40
Methanol	69,54,51*
Methyl Ethyl Ketone	48*
2-Propanol	15*

*Successive regeneration cycles.

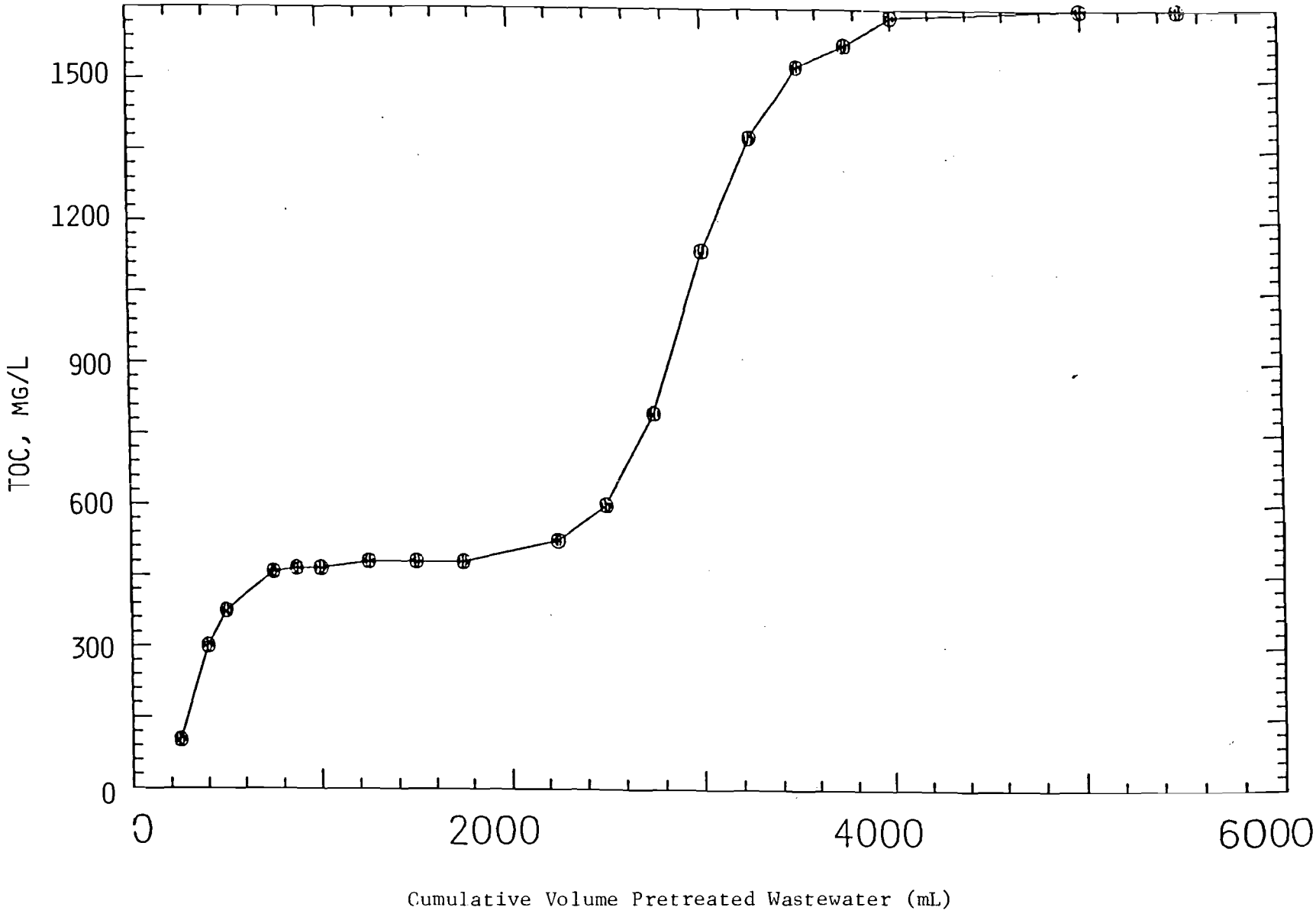

Fig. 54 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent. Adsorption-Regeneration Study

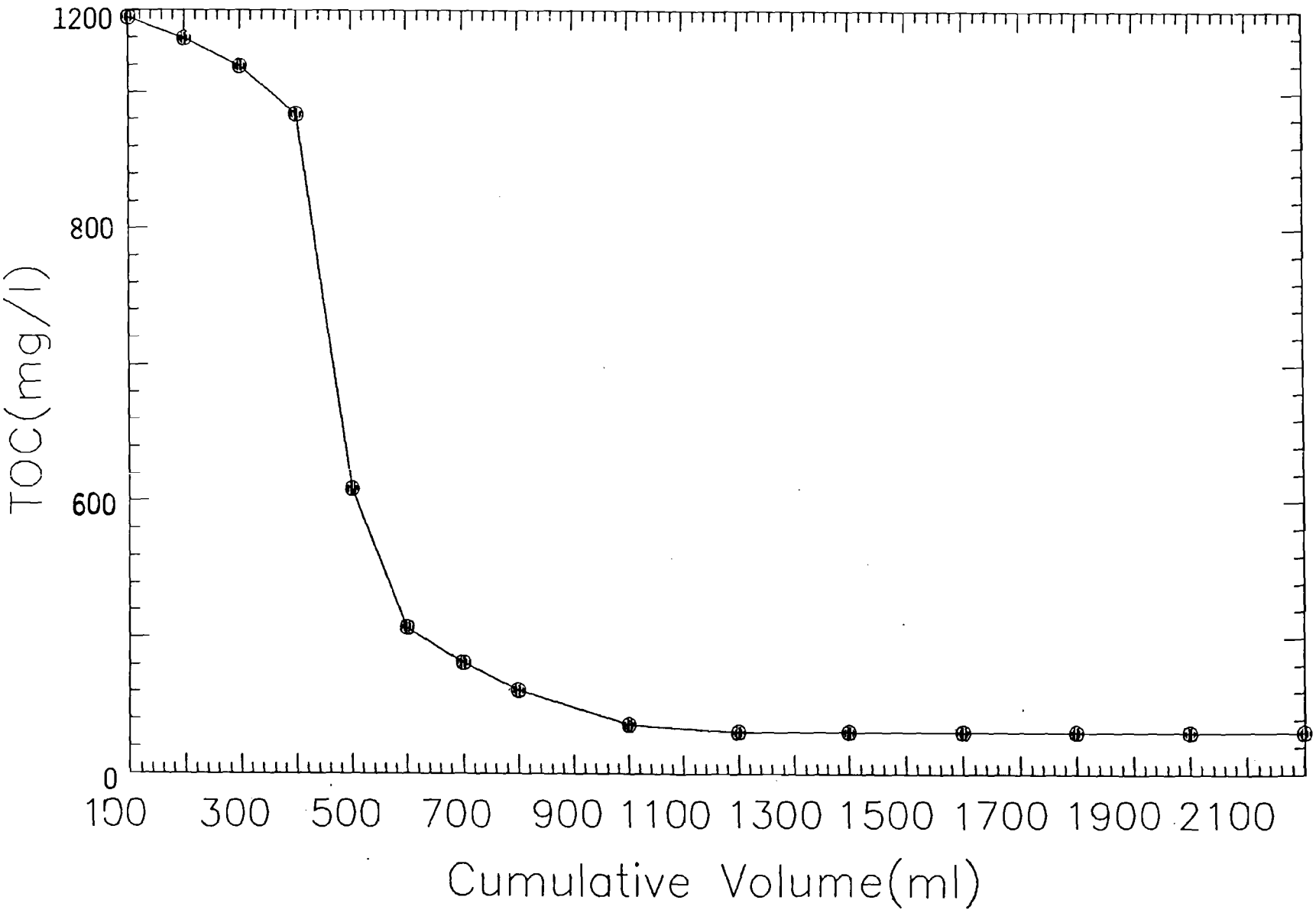

Fig. 55 Solvent Regeneration of Exhausted Activated Carbon Using Sodium Hydroxide (0.1M).

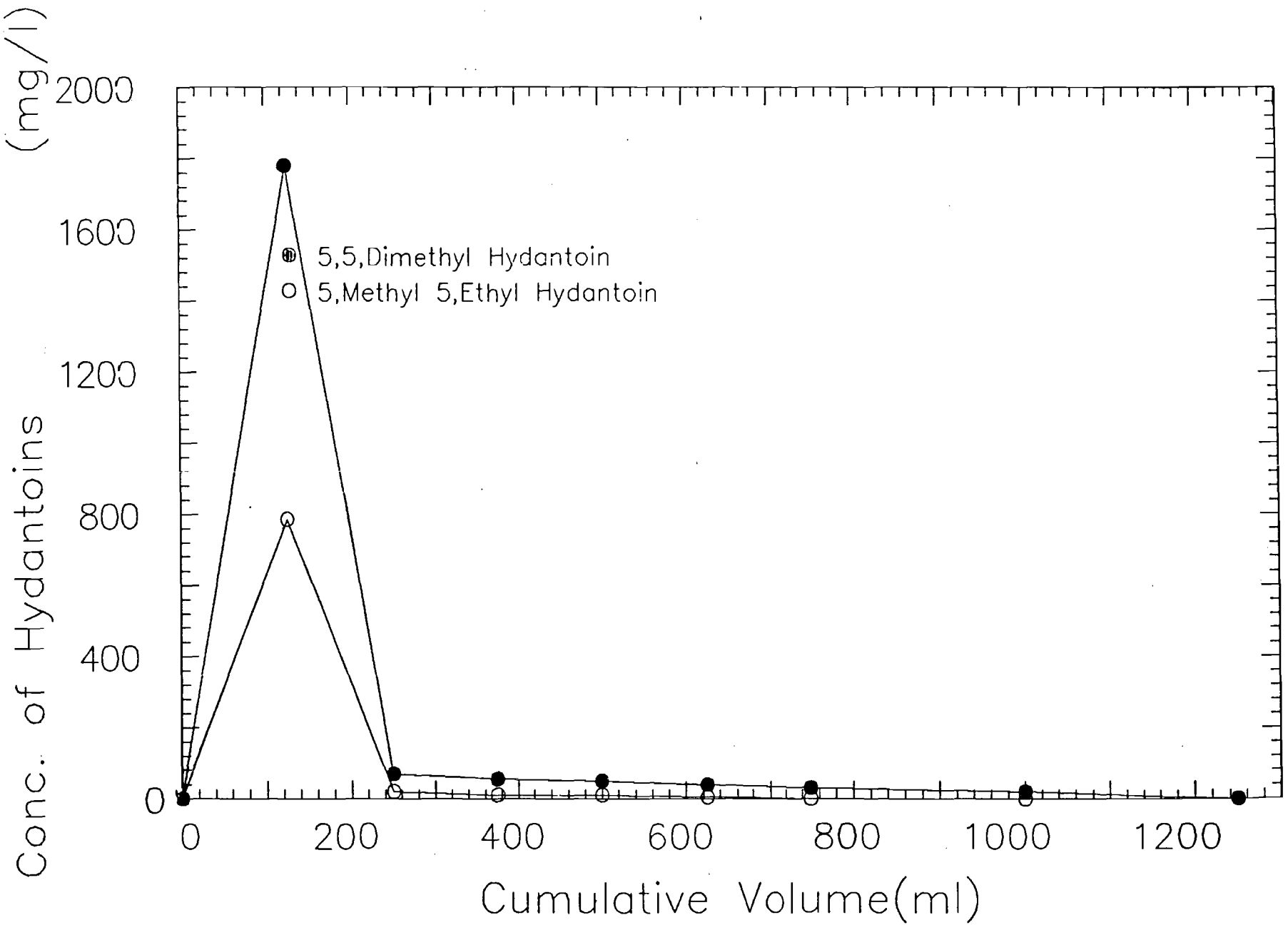

Fig. 56 First Regeneration of Exhausted Activated Carbon Using Methanol.

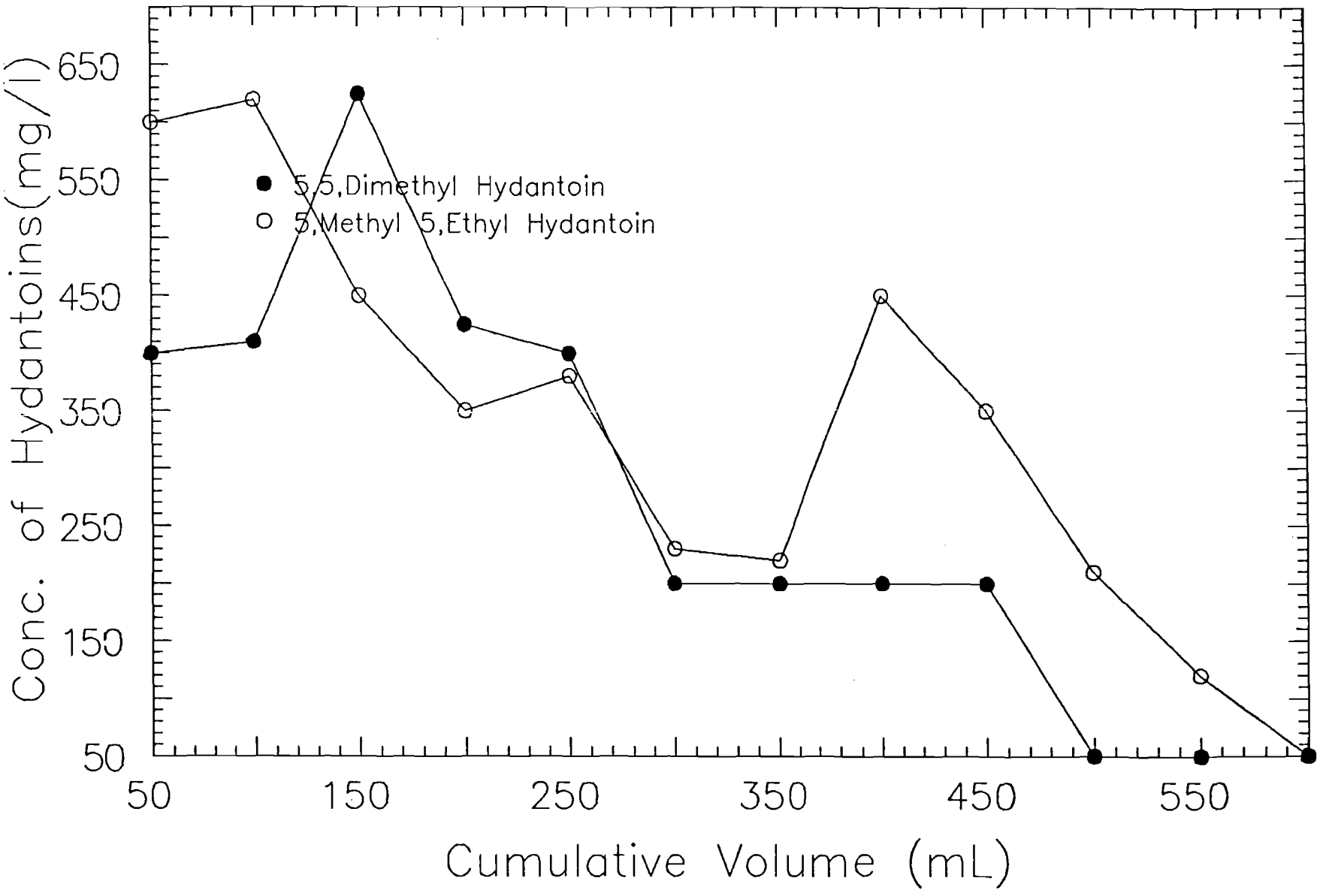

Fig. 57 Second Regeneration of Exhausted Activated Carbon Using Methanol.

SUMMARY

Dilute (~10%) coal gasification effluent was successfully treated biologically for the removal of organic carbon and ammonia. The complete treatment train consisted of a two-stage anaerobic activated carbon filter for organic carbon removal followed by a single sludge nitrification system for conversion of ammonia nitrogen to nitrate-nitrogen and finally conversion of nitrate-nitrogen to nitrogen gas in a biological denitrification system.

After an extended period of operation on ~10% coal-gasification effluent inhibition of both the anaerobic and the nitrification systems occurred. Inhibition of the anaerobic system was partially overcome by replacement of a portion of the granular activated carbon in the filter. Continued periodic replacement of the activated carbon was required to maintain a viably operating anaerobic filter. Nitrification inhibition was eliminated by either addition of powdered activated carbon to the aeration basin or by the periodic replacement of a portion of the granular activated carbon in the anaerobic filter.

Batch inhibition studies indicated that substituted pyridines (picolines) were inhibitory to the anaerobic system. Inhibition of the nitrification system was attributed to the increase in effluent cresol concentrations from the anaerobic filter as the adsorption capacity of the granular activated carbon was exceeded.

Carbon adsorption-solvent regeneration studies on pure compounds (hydantoin and substituted hydantoins), and on solvent extracted-ammonia stripped coal gasifier effluents indicated that the limited adsorption capacity for the hydantoins coupled with incomplete regeneration of the exhausted carbon would limit the utility of this method as a treatment process for the removal of organic carbon from pretreated coal gasification effluent.

APPENDIX A

TREATMENT SYSTEMS

TREATMENT SYSTEMS

The systems used in the treatment of coal gasifier effluent and pretreated coal gasifier effluent are described in the following sections with pertinent data for each system.

Two-Stage Anaerobic Reactor System

The two-stage pilot-scale anaerobic filter columns employed in this study (Figure 58) consist of two identical Plexiglas columns, each having a height of 183 cm and an internal diameter of 10 cm. Each of these columns was connected to a 20-cm-long inverted conical base to accommodate the influent. The upper end of the first-stage column was connected to a similar conical effluent section also equipped to allow gas collection while the second-stage column was connected to a 30-cm-long by 15-cm-i.d. expansion chamber to allow for the settling of gas-bound carbon particles. A 13-cm-diam concentric Plexiglas water jacket was placed around each column to maintain constant temperature conditions (35 ± 0.5°C). The water jackets were connected, in series, to a constant temperature water bath (Lauda model B, Westbury, NY).

The first-stage filter was packed with Raschig rings (0.5-in. nominal size) to a depth of 173 cm, whereas the second-stage fluidized bed column was packed to a depth of 125 cm with 10 x 20 U.S. mesh Filtrasorb 400 granular activated carbon (Calgon Corp., Pittsburgh, PA). A ½-hp stainless-steel centrifugal pump (Teel Pump, Dayton, OH) was used for recirculation and to fluidize the granular activated carbon to minimize gas entrainment, to provide dilution, and to furnish buffering capacity by recirculating the system effluent at a high rate compared to flow through the system.

Anaerobic Columns in Series

The anaerobic activated carbon columns in series were of identical size and design of those used in the two-stage anaerobic reactor system and are depicted in Figure 59.

Nitrification Reactor

The biological nitrification system used in this study (Figure 60) was a single-stage, completely mixed activated sludge unit which consisted of an aeration basin (18.5-cm internal diameter, 40-cm height, 10.8-L volume) was fed with a variable flow positive displacement pump. Compressed air was controlled by a pressure regulator, metered with a rotameter, and supplied from a diffuser at the bottom of the basin. The clarifier consisted of a plexiglas column (10-cm internal diameter by 80-cm height, 6.6-L volume) with an inverted c nical base and a rotating sludge scraper to minimize sludge adhering to the wall of the clarifier or logging the conical bottom. A tubing pump was used for sludge recycle to the aeration basin. Both the tubing pump and scraper were operated intermittently by a timer. The system was operated indoors at ambient temperature (19 to 23°C) for 1 year.

Denitrification Reactor

Suspended growth denitrification of anaerobically treated and nitrified wastewater with cell recycle was performed in a 10-L covered reactor. The reactor was coupled to a small aeration basin which was used to remove nitrogen gas prior to clarification, as presented in Figure 61. Settled solids were recycled to maintain the proper solids retention time. Influent (nitrification effluent and methanol solution) was applied to the

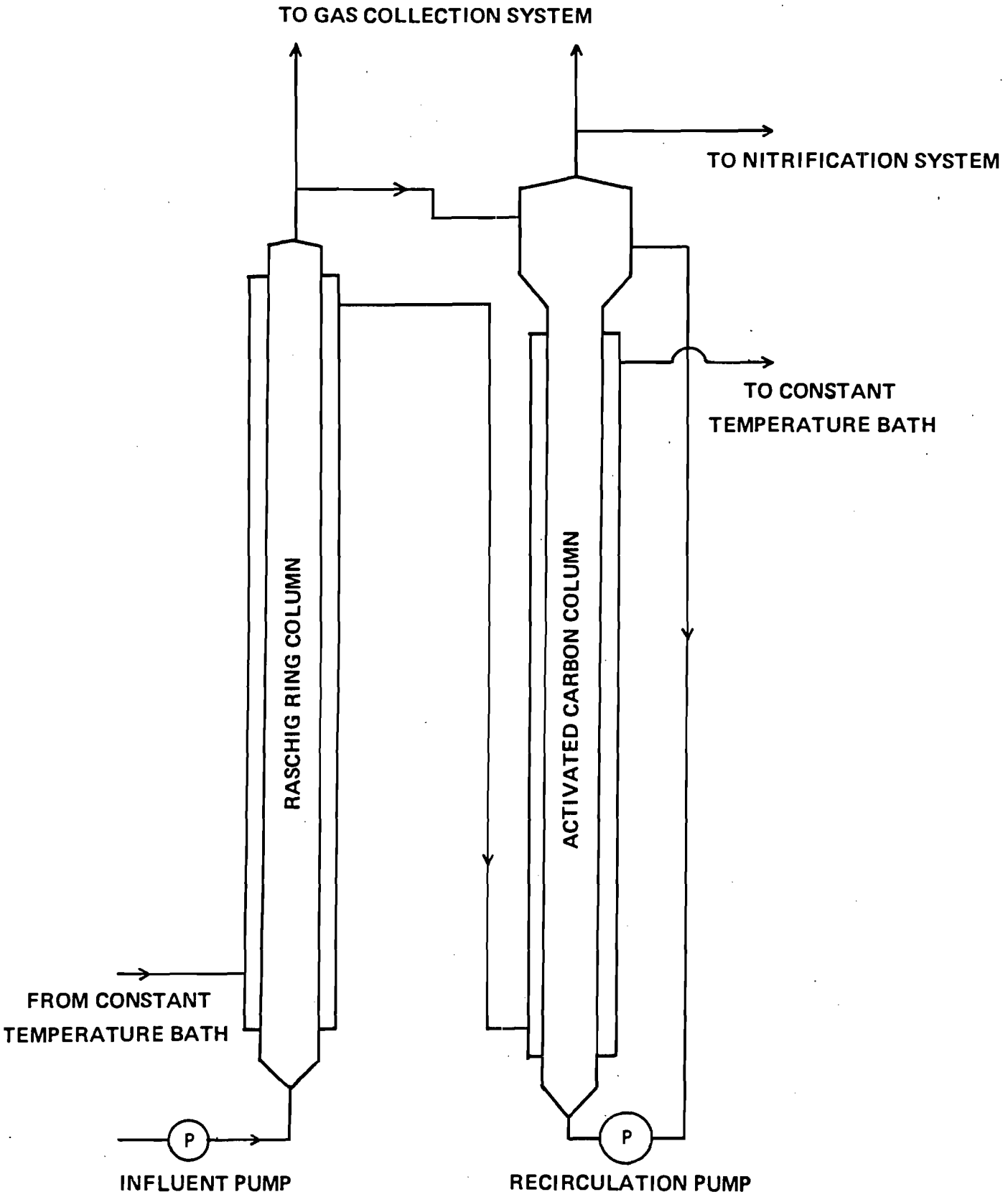

Fig. 58 Two Stage Anaerobic Activated Carbon Filter.

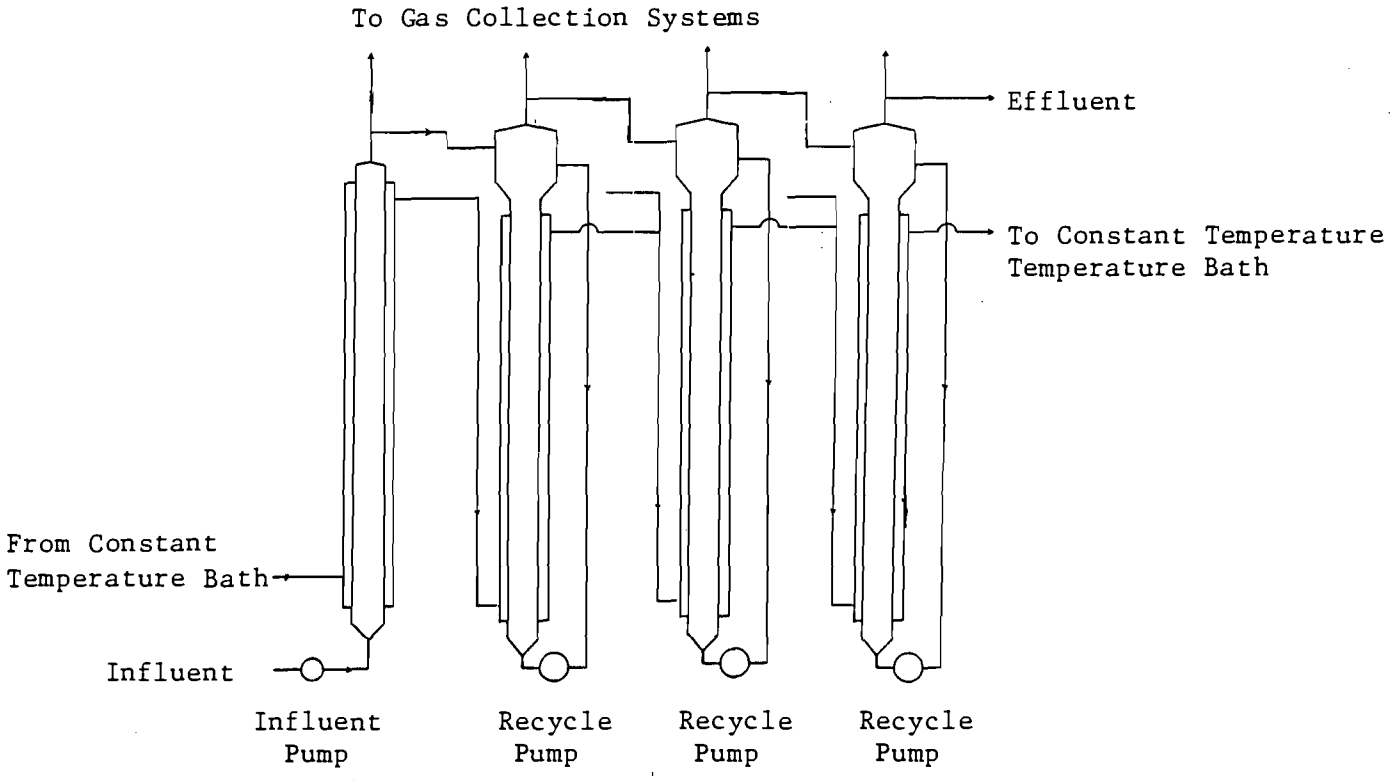

Fig. 59 Anaerobic Activated Carbon Filter in Series.

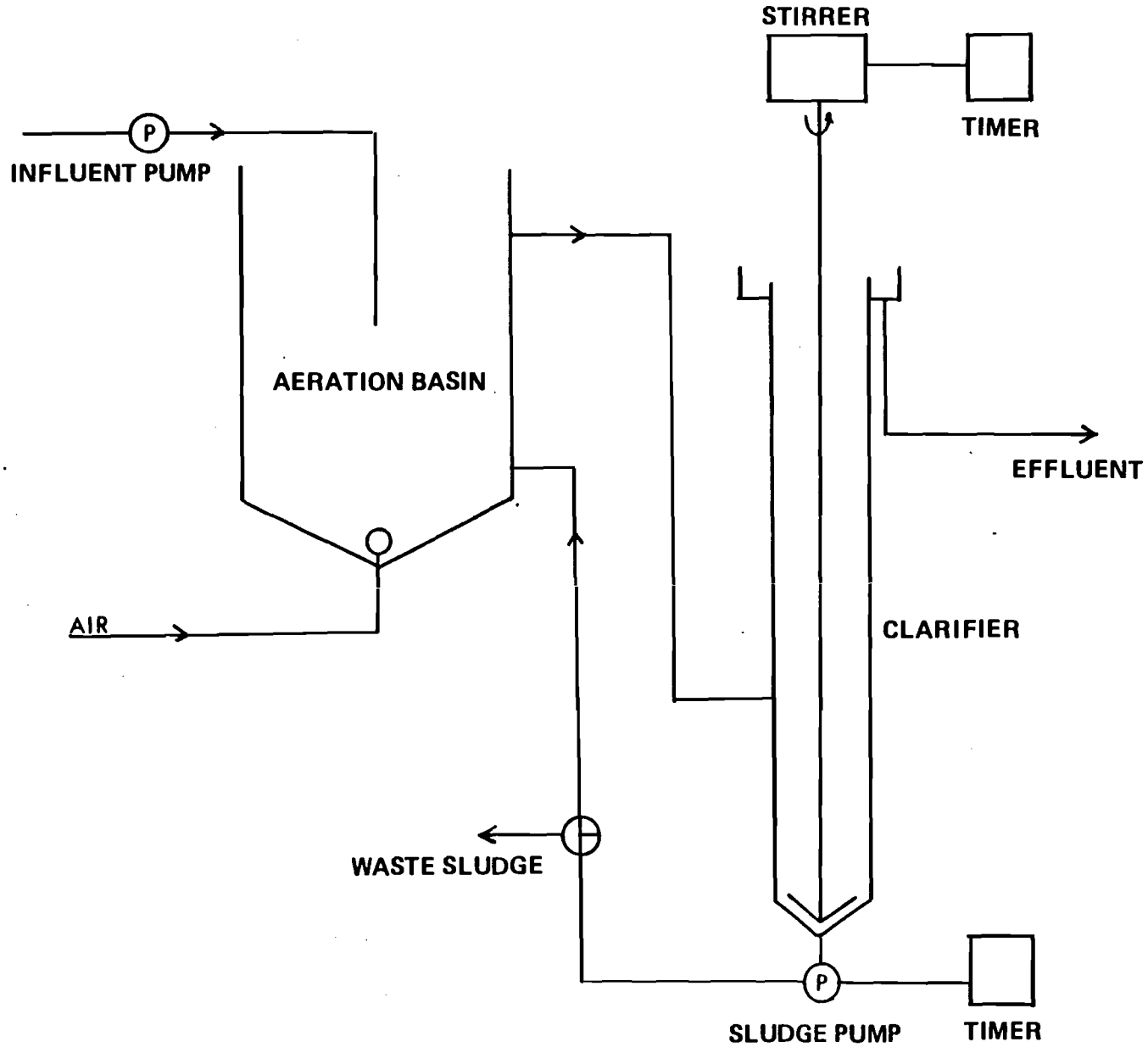

Fig. 60 Biological Nitrification System

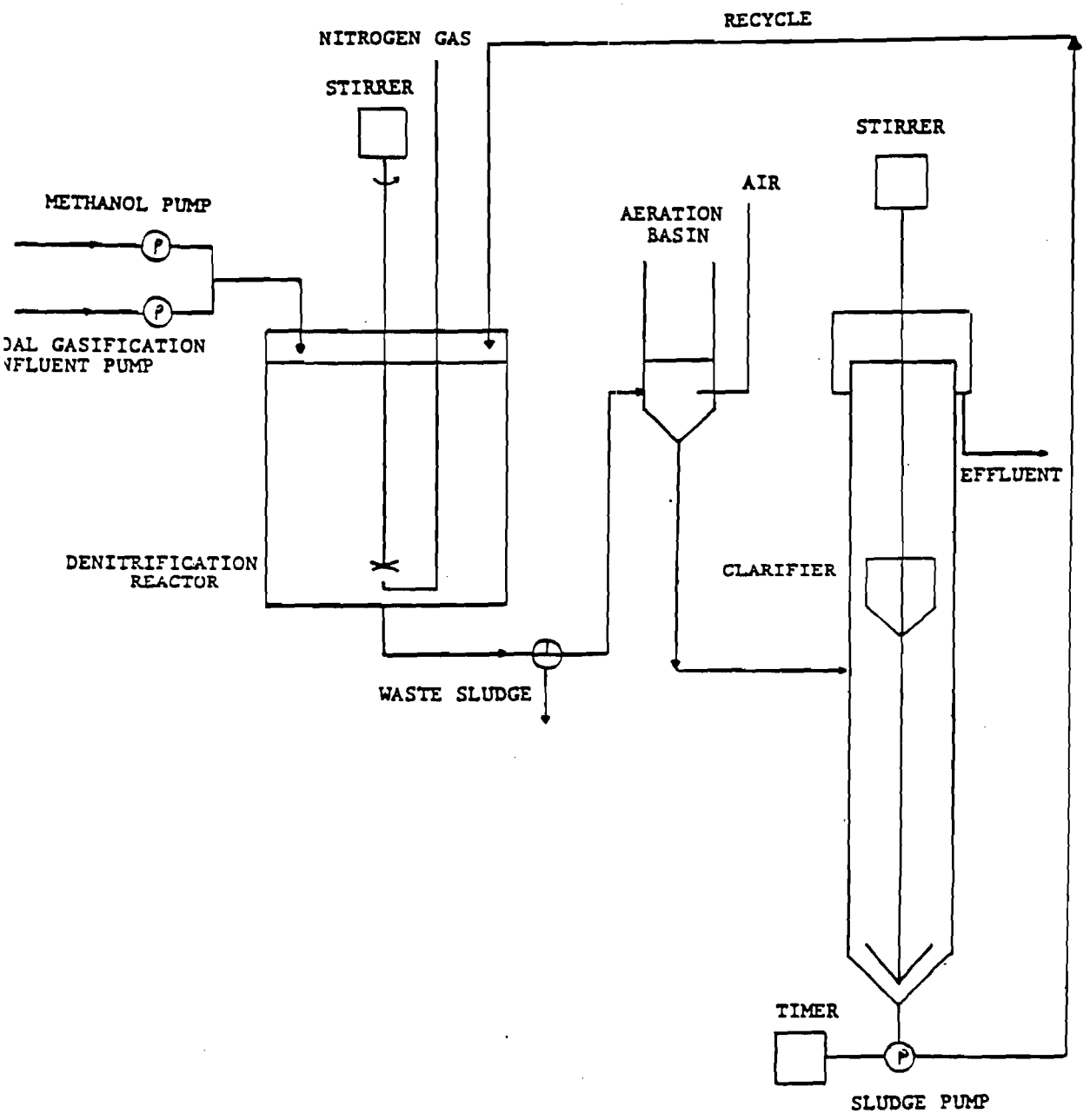

Fig. 61 Biological Denitrification System.

denitrification reactor from two reservoirs equipped with variable-speed, positive-displacement pumps (Fluid Metering, Inc., Oyster Bay, NY). An airtight cylindrical acrylic reactor served as the denitrification chamber (dimensions are given in Table 23). The reactor was equipped with a variable speed stirrer, which was continuously operated at 2500-3000 rpm. Nitrogen gas was supplied at a rate of 80-109 mL/min to strip oxygen from the influent and to exclude air from the reactor. The effluent from the denitrification reactor was fed into an aeration basin (see dimensions in Table 23). Pressurized air was introduced into the aeration basin through an air diffuser at a rate of 120-160 mL/min. The effluent from this unit then flowed to the clarifier (see dimensions in Table 23). The clarifier had an inverted conical base and settled solids were recycled using a peristaltic tubing pump (Cole Parmer, Chicago, IL). The pump was controlled to recycle solids at a rate of approximately 100 mL/min for three minutes at fifteen-minute intervals resulting in a recycle ratio of 2.9. The clarifier was equipped with two wall scrapers. One was located 37 cm from the top of the clarifier and the second one was at the bottom of the clarifier. In addition, the stirrer was connected to a motor speed controller (Bodine Electric Co., Chicago, IL) and was rotated at a rate of 1 rpm to minimize the quantity of sludge adhering to the walls of the clarifiers or bridging in the conical bottom.

Overall Treatment System

Figure 62 is a schematic diagram for the overall biological treatment system utilized in the study for treating UNDERC effluent.

Inhibition Studies

Batch inhibition studies were carried out in 125 mL serum bottles using a modified Hungate technique. The bottles were flushed with a carbon dioxide-nitrogen mixture (30% CO_2, 70% N_2) prior to and during filling and inoculation.

Adsorption-Regeneration Studies

Glass columns (Figure 63) (2.5-cm i.d. x 30-cm long) equipped with a positive displacement pump and operated in a upflow mode were used for the adsorption-regeneration cycle studies. Two reservoirs were coupled to the pump via a 3-way stopcock in order to switch from wastewater to regenerant and vice versa without having to shut down the system or interrupt flow through the column.

An automatic time-operated fraction collector was used to obtain samples for analysis.

Table 23. Dimensions of the Denitrification Reactor System

Reactor System	Internal Diameter cm	Height cm	Total Volume L	Liquid Volume L	HRT* Hours
Denitrification Reactor	20	38	11.9	10	24
Aeration Basin	6.2	30.5	1.0	0.25	0.5
Clarifier	11.0	100	10.2	10.2	24

*At flow of 10 L/d

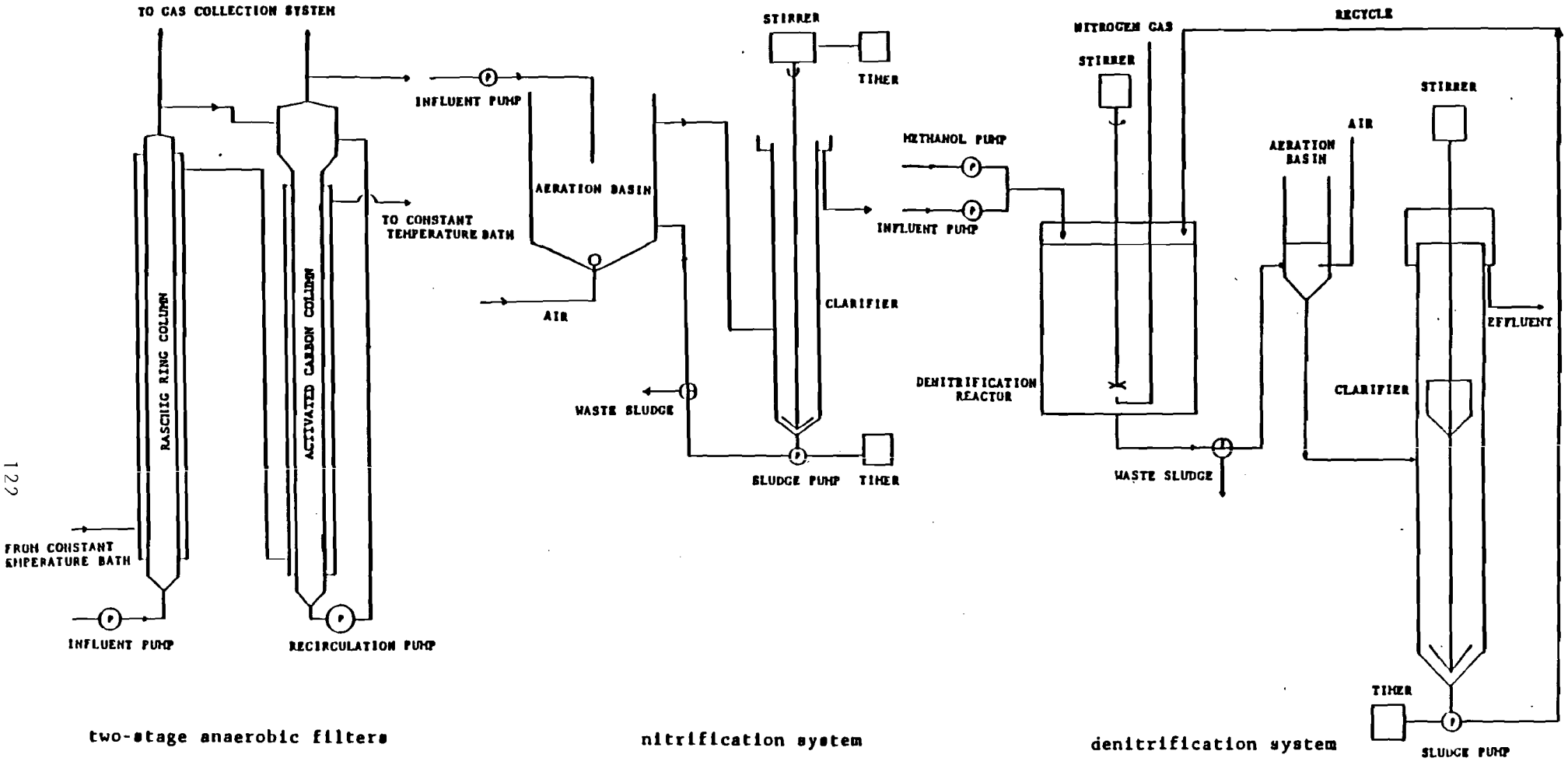

Fig. 62 Overall Processes Used to Treat Coal Gasification Effluent.

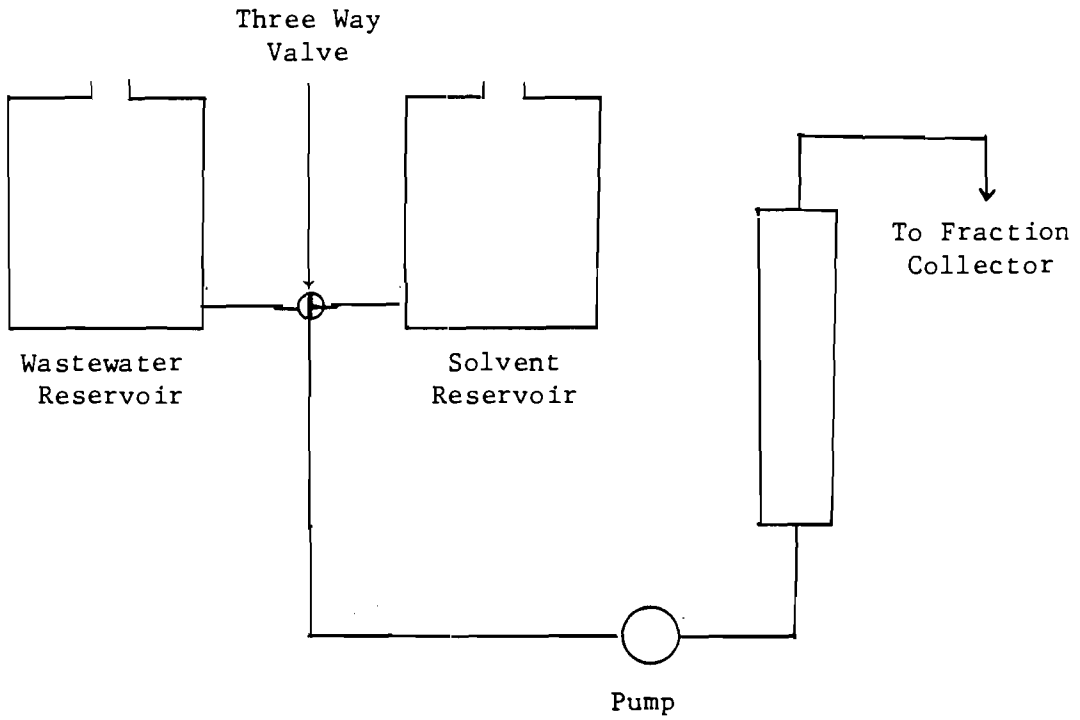

Fig. 63 Carbon Adsorption - Solvent Regeneration System.

APPENDIX B

ANALYTICAL METHODS

PARAMETER	METHOD
pH	potentiometric, Standard Methods[35] 423
Alkalinity	Standard Methods 403, endpoint pH = 3.5
ORP	potentiometric, platinum electrode
CN^-	Standard Methods 412E
NH_3-N	Standard Methods 417G
TKN-N	acid digestion (H_2SO_4-$HClO_4$) followed by Standard Methods 417G
PO_4^{-3}-P	Standard Methods 424G
Suspended solids	Standard Methods 209C
Volatile solids	Standard Methods 209D
Total organic carbon	Standard Methods 505A
Chemical oxygen demand	Standard Methods 508A
NO_2^--N	Standard Methods 419
NO_3^--N	Standard Methods 414D
Metals	HNO_3, H_2O_2 oxidation followed by atomic absorption analysis
Phenol, cresols	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 0.1% SP-10000 on 80/100 mesh Carbopack C (Supelco, Inc.). 195°C, nitrogen carrier at 20 mL/min, direct aqueous injection, internal standard benzyl alcohol, FID
Volatile acids	gas chromatography, 1.2-m long glass column, 2-mm i.d., packed with 3.0% Carbowax 20 M, 0.5% H_3PO_4 on 60/80 mesh Carbopack B (Supelco, Inc.). Temperature program 100°C for 2 min to 150°C at 4°C/min and hold for 15 min. Nitrogen carrier 20 mL/min, direct aqueous injection, internal standard 1-butanol or 2-propanol, FID.
Gas composition	gas chromatography, 75-cm long aluminum column, 0.64-cm i.d., packed with 30% DEHS on 60/80 mesh ColumnPak (Fisher Scientific Co.) followed by a 1.8-m long aluminum column 0.48-cm i.d. packed with 60/80 mesh 5A Molecular Sieve (Fisher Scientific Co.) 25°C, Helium carrier 80 mL/min, TCD.

Hydantoins, individual pure solutions	UV/VIS spectroscopy and/or TOC hydantoin, λ_{max} 193 nm; 5-ethyl-5-methyl hydantoin, λ_{max} 193 nm; 5,5-dimethylhydantoin, λ_{max} 198 nm.
Mixtures of hydantoins	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 3% AT-1000 on 100/120 mesh Chromosorb W-HP (Alltech Assoc.) 225°C, nitrogen carrier 40 mL/min, FID, calibration curve.
Other organic constituents	solvent extraction and concentration followed by gas chromatographic separation using mass spectrometry for identification.

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